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CONSTRUCTION GRANTS PROGRAM
INFORMATION
EPA-430/9-76-017c

VOLUME III

PB 266 783

appendix 8

FEDERAL GUIDELINES

STATE AND LOCAL PRETREATMENT PROGRAMS

JANUARY 1977

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WASHINGTON, D.C. 20460

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The guidelines are a revision of the previous guidelines, "Pretreatment of Pollutants Introduced Into Publicly Owned Treatment Works." Contained in this revision is additional technical information on pollutants which may interfere with or pass through publicly owned treatment works. Also, guidance is presented to assist State and local governments in developing their own pretreatment programs to comply with NPDES permit conditions.

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JANUARY 1977

U.S. ENVIRONMENTAL PROTECTION AGENCY
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U.S. ENVIRONMENTAL PROTECTION AGENCY

FOREWORD

In response to the Federal Water Pollution Control Act Amendments of 1972 (P.L. 92-500), this country has undertaken an unprecedented program of cleaning up our Nation's waters. There will be a substantial investment by Federal, State, and local governments as well as by private industry in treatment works to achieve the goals of the Act. It is important that this investment in publicly owned treatment works (POTW's) be protected from damage and from interference with proper operation, and that receiving waters be protected from pollutants which may pass through the POTW.

These guidelines were developed by the Environmental Protection Agency in accordance with Section 304(f) of the Act for the purpose of assisting States and municipalities in carrying out programs under Section 402 including NPDES permit requirements. It is important to note the clear requirements in the Act that there be both national pretreatment standards, Federally enforceable, and pretreatment guidelines to assist States and municipalities in developing local pretreatment requirements. The Environmental Protection Agency encourages the establishment of local pretreatment requirements, tailored to local conditions.

The guidelines are a revision of the previous guidelines, "Pretreatment of Pollutants Introduced Into Publicly Owned Treatment Works." Contained in this revision is additional technical information on pollutants which may interfere with or pass through publicly owned treatment works. Also, guidance is presented to assist State and local governments in developing their own pretreatment programs to comply with NPDES permit conditions. The guidelines are the result of extensive reviews and numerous field trips and discussions with EPA Regional Offices, industry, city, regional, State and interstate agencies. We are extremely grateful for the cooperation of those who assisted in the preparation of the guidelines.

/s/ John Quarles

DEC 22 1976

The Administrator

Acting

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INTRODUCTION

Purpose and Scope

The purpose of this volume is to provide data concerning the major industries that may be contributing wastewater to publicly owned sewer systems and treatment works. Included are descriptions of thirty-four major industrial categories which were partially established by the Federal Water Pollution Control Act Amendments of 1972 (PL 92-500) and further developed by the Effluent Guidelines Division of the Environmental Protection Agency.

The summary for each industrial category includes the following information:

1. A general industry description of the products, raw materials, waste characteristics, and Standard Industrial Classification code numbers applicable to each industry.

2. The categorization and subcategorization developed for the industry by the EPA in the effluent guidelines program.

3. Process descriptions, based upon the subcategorization established for the industry, with the major sources of wastewater delineated for each process.

4. Waste characterization, including tables of concentration and production based data for the pollutants associated with each industry.

5. Control and treatment technology including the in-plant controls and end-of-pipe treatment utilized and available in each industrial category.

The information presented herein was summarized from the Development Documents prepared by the Effluent Guidelines Division of the EPA. A list of these reference documents is attached at the end of this volume.

The waste characterization tables provide broad ranges of values which represent data from a cross-section of each industry throughout the country. As a result, a particular plant of interest may not be adequately characterized by the values shown. The purpose of the tables is to furnish general background information on the waste chracteristics of most plants in the industry. For precise data, sampling of plant effluent should be employed.

In many cases, industrial plants utilize processes or manufacture products encompassing more than one industrial category or subcategory. In those instances, weighted averages of the data should be used to represent the plant effluent. Sampling at strategic points can be most useful in establishing the effluent quality from multi-product or multi-process plants.

Table i-1 summarizes the significant pollutant parameters present in the effluent from each of the 34 major industrial categories. In some cases, a particular parameter may only be significant for one subcategory of the industry. To determine the applicable subcategory, reference should be made to the summary for the specific industry in question. For further information on a particular industry, the Development Document for that industry should be consulted.

Pretreatment

The information contained in the individual industrial summaries can be utilized to identify conditions requiring careful evaluation when establishing pretreatment requirements for a specific industry or when designing joint treatment facilities. The wastewater characterization data is also a guide for developing a wastewater testing program for a particular industry. The control and treatment technologies identified for each industry indicate in-plant control techniques and end-of-pipe treatment processes available for use by industrial dischargers.

Pretreatment of industrial wastes before discharge into a POTW system is usually a case-by-case problem. In general, it is usually required by the EPA, States or municipalities to prevent the discharge of pollutants which may interfere with or pass through municipal treatment plants, as described in Volume 1. However, pretreatment decisions are frequently dictated by the specific circumstances of each individual situation. An industrial facility discharging directly to navigable waters may decide to join a POTW system and pretreat after a technical and economic analysis because it is the most cost-effective alternative. Similarly, industries in the system may opt for pretreatment where a small investment in pretreatment facilities would result in a significant reduction in the pollutant loading and a corresponding large reduction in surcharge or user charge fees.

In all cases, in-plant control measures which might reduce or eliminate the need for pretreatment facilities should first be examined before embarking on a pretreatment program. In many circumstances, a thorough examination of plant operational practices, recycle alternatives, and other water conservation or reuse possibilities can significantly reduce pollutant loads.

TABLE 1-1
SUMMARY OF SIGNIFICANT POLLUTANT PARAMETERS FOR MAJOR INDUSTRIES

Industry	BOD	TSS	TDS	COD	pH	Cyanide	Color	Oil and Grease	Phosphorus	Ammonia	Fluoride	Chrome	Copper	Lead	Zinc	Cadmium	Iron	Nickel	Arsenic	Sulfide	Manganese	Mercury	Nitrate Nitrogen	Phenol	Boron	Selenium
Dairy	X	X	X	X	X		X		X																	
Grain Mills	X	X	X	X	X				X																	
Canned and Preserved Fruits and Vegetables	X																									
Canned and Preserved Seafood	X	X		X				X																		
Sugar	X	X	X	X	X																					
Textile	X	X	X	X	X		X	X				X														
Cement																										
Feedlots	X	X	X	X						X																
Metal Finishing & Electroplating		X			X	X			X		X	X	X	X	X	X	X	X								
Organic Chemicals		X	X	X				X		X														X		
Inorganic Chemicals		X	X	X	X							X										X				
Plastics and Synthetics	X	X	X	X	X			X		X	X	X												X		
Soap and Detergents	X	X	X	X	X			X																		
Fertilizer		X			X				X	X	X															
Petroleum	X							X		X		X			X					X				X		
Iron and Steel	X					X		X		X				X	X					X	X					
Nonferrous Metals		X	X		X			X			X		X	X	X	X			X							X
Phosphates		X	X		X				X		X				X		X		X							
Steam Electric Power		X			X			X	X			X	X		X		X							X		
Ferroalloys		X			X	X				X		X					X				X			X		
Leather Tanning & Finishing	X	X		X	X			X				X								X						
Glass	X	X	X	X	X		X	X	X															X		
Asbestos	X		X	X	X																					
Rubber	X	X	X	X				X						X	X											
Timber	X	X		X	X		X	X																X		
Pulp and Paper	X	X			X		X																			
Builders Paper	X	X			X																					
Meat	X		X	X			X	X																		
Paint and Ink	X	X	X	X	X		X	X				X	X	X	X	X	X					X				
Auto and Other Laundries	X	X	X	X	X			X				X	X	X	X	X	X	X								
Water Supply		X	X	X			X				X															
Steam Supply		X			X			X	X			X	X		X		X							X		
Misc. Foods and Beverages	X	X		X	X			X																		
Misc. Chemicals	X	X	X	X	X	X		X				X			X		X						X	X	X	

Accordingly, contained in each industrial summary is a discussion pertaining to available in-plant control technology for the industry in question.

Pretreatment considerations may differ depending on whether the pollutants to be controlled are susceptible to treatment in a POTW. For compatible pollutants, pretreatment would generally be employed because it is the most cost-effective alternative, or because the POTW does not have available design capacity to treat the wastes. Even in cases where the municipality has available design capacity to accept an industrial discharger without pretreatment, the industry should still perform some sort of break-even analysis to determine if pretreatment is cost-effective. An example of this type of analysis for the meat packing industry is contained in Reference A-33. In cases where design capacity is not available, the municipality may elect to assign waste load allocations to each industrial discharger, thus fixing the required pretreatment. Waste load allocation will in these cases be necessary to meet the municipality's NPDES permit requirements.

Pretreatment for compatible pollutants can take a variety of forms, including:

1. Coarse solids separation
2. Grit removal
3. Equalization
4. Neutralization
5. Dissolved air flotation
6. Sedimentation
7. Biological treatment
    a. Activated sludge systems
    b. Trickling filter systems
8. Physical-Chemical treatment
    a. Chemical coagulation
    b. Filtration
    c. Activated carbon adsorption

Most pretreatment systems should include some form of coarse solids separation, grit removal, and equalization. Equalization may be required for either flow, pollutant load or both. It is particularly important in the prevention of excessive discharge and the imposition of shock loads on POTW systems. Similarly, neutralization is a significant unit process in pretreatment operations, to avoid possible process upset or damage to POTW facilities by highly acidic or alkaline wastes.

Dissolved air flotation and sedimentation are utilized to remove suspended solids and floatable material such as oil and grease. Dissolved air flotation is particularly useful in industries where oil and grease presents problems in the discharge of wastewater to municipal systems. Biological treatment is used in pretreatment operations to reduce BOD loading prior to discharge to a municipal sewer. The desired reduction is highly variable, and depends upon economic considerations and available capacity in the treatment facility. In many instances, a BOD reduction to 200-250 mg/l is sought in pretreatment facilities to produce an effluent which simulates domestic sewage. Frequently, high rate activated sludge systems or roughing filters are utilized in pretreatment systems to effect the desired BOD reduction in the most cost-effective manner. Physical-chemical treatment may be employed for suspended solids and BOD removal where technical and economic factors favor this alternative over conventional primary and biological treatment processes.

Pretreatment for incompatible pollutants can also take a variety of forms, including:

1. Coarse solids separation
2. Grit removal
3. Equalization
4. Neutralization
5. Dissolved air flotation
6. Sedimentation
7. Filtration
8. Chemical precipitation and coagulation
9. Activated carbon adsorption
10. Chemical conversion

The degree of pretreatment required for incompatible pollutants is primarily determined by the level of discharge into the municipal system required to prevent interference or pass through, as outlined in Section E of Volume I. The treatment of incompatible pollutants is frequently concerned with the removal of inorganic suspended and dissolved solids as opposed to the organic nature of compatible pollutants. Consequently, the unit processes concerned with suspended solids removal such as sedimentation and dissolved air flotation involve the same considerations as with compatible pollutants. Similarly, equalization and neutralization are equally important in treating incompatible pollutants to prevent shock loading and possible process upset or damage to POTW facilities.

The distinguishing element in treating incompatible pollutants is the removal of inorganic dissolved solids, particularly metals. The most common processes employed are chemical precipitation and coagulation and chemical conversion.

In precipitation and coagulation, the dissolved pollutant reacts with the chemical agent used to form an insoluble precipitate. The precipitate is allowed to settle and is removed as a sludge. In chemical conversion, the pollutant in question is converted to another less harmful form or to another substance. Typical of this type of treatment is the reduction of hexavalent chromium to the trivalent form and the destruction of cyanide. Activated carbon adsorption may be used to remove dissolved organic pollutants which are not susceptible to treatment in POTW's.

In summary, pretreatment must be evaluated on a case-by-case basis within the context of cost-effectiveness and applicable technical factors. Pretreatment considerations depend primarily upon whether the wastewater in question is compatible or incompatible with POTW systems. In either case, a variety of unit processes are available to a particular industrial facility for pretreatment of wastewater prior to discharge to a municipal sewer.

1. General Industry Description

The dairy processing industry manufactures various food products utilizing milk as a base. In addition, a limited number of non-milk products such as fruit juices are processed in some plants.

There are about 20 different types of products manufactured by the industry. A substantial number of plants in the industry engage in multi-product manufacturing, and product mix varies broadly among such plants.

The Dairy Product Processing Industry includes Standard Industrial Classifications (SIC) 2021, 2022, 2023, 2024, 2026 and 5043.

2. Industrial Categorization

Subcategory	Designation
Receiving Stations	A
Fluid Products	B
Cultured Products	C
Butter	D
Cottage Cheese and Cultured Cream Cheese	E
Natural Cheese and Processed Cheese	F
Ice Cream Mix	G
Ice Cream, Novelties, and other frozen desserts	H
Condensed Milk	I
Dry Milk	J
Condensed Whey	K
Dry Whey	L

3. Process Description

Figure 8-1-1 is a flow diagram which shows a process representative of the industry. The industry includes the following operations: the receiving and storage of raw materials, processing of raw materials into finished products, packaging and storing of finished product, and a group of ancillary operations (e.g., heat transfer and cleaning) only indirectly involved in processing of materials.

Facilities for receiving and storing raw materials consist of a receiving area, transfer equipment, and large refrigerated tanks for storage. Wastes arise from leaks, spills and equipment wash outs. Under normal operations and with good housekeeping, receiving and storage of raw materials are not a major source of waste load.

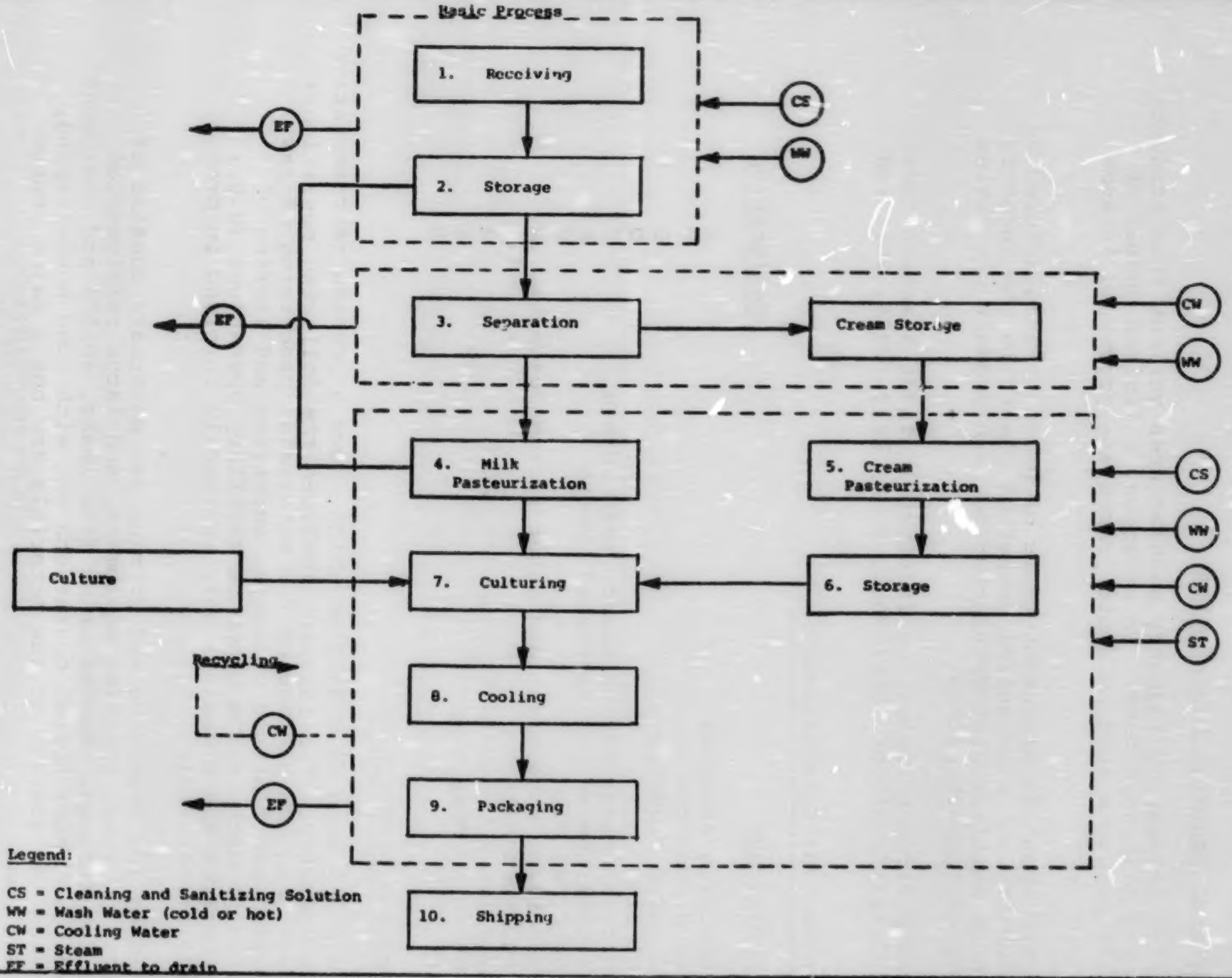

Basic Process
1. Receiving
2. Storage
3. Separation
Cream Storage
4. Milk Pasteurization
5. Cream Pasteurization
6. Storage
7. Culturing
8. Cooling
9. Packaging
10. Shipping
Culture
Recycling
CS
WW
CW
ST
EF
Legend:
CS = Cleaning and Sanitizing Solution
WW = Wash Water (cold or hot)
CW = Cooling Water
ST = Steam
EF = Effluent to drain

FIGURE 8-1-1
CULTURED PRODUCTS
DAIRY PRODUCTS PROCESSING

The initial operations of clarification, separation and pasteurization are common to most plants and products. Clarification (removal of suspended matter) and separation (removal of cream) generally are accomplished by using large centrifuges of special design. In some older installations clarification and separation are carried out in separate units that must be disassembled for cleaning, sanitizing, and sludge removal. In most plants clarification and separation are accomplished by a single unit that automatically discharges the sludge and can be cleaned and sanitized without disassembly (cleaned in place, or CIP).

Following clarification and separation, those materials to be subjected to further processing within the plant are pasteurized. Pasteurization is accomplished in a few older plants by heating the material for a fairly long period of time in a vat (vat pasteurization). In most plants pasteurization is accomplished by passing the material through a unit where it is first rapidly heated and then rapidly cooled by contact with heated and cooled plates or tubes (high temperature short time or HTST pasteurization).

After the initial operations, the processes and equipment employed become dependent on the product to be manufactured. The processes employed for the manufacture of various products include churning, homogenizing, culturing, condensing, and drying The finished products are then packaged, cased and sent to storage for subsequent shipment. The flow diagram shown in figure 8-1-1 is representative of many processes in this industry.

The product manufacture and packaging areas of a plant are the major sources of wastes. These wastes result from spills and leaks, wasting of by-products (e.g., whey from cheese making), purging of lines during product change, product washing, and equipment washups. Wastes from storage and shipping result from the rupture of containers due to mishandling and should be minimal.

4. Wastewater Characterization

Tables 8-1-1 and 8-1-2 show typical waste characteristics for the dairy industry. A significant characteristic of the waste streams of all dairy plants is the marked fluctuations in flow, strength, temperature, etc. due to daily and seasonal variations. Relatively clean water from condensers, refrigeration compressors, milk coolers and air conditioning systems may be a substantial portion of the total wastewater from a dairy plant. The major sources of wastewaters from the dairy industry are:

1. Wash and rinse water from washups.
2. Unrecovered by-products.
3. Entrainment from evaporators.
4. Sewering of spoiled or damaged products.

TABLE 8-1-1

DAIRY PRODUCTS

RAW WASTEWATER CHARACTERISTICS

Parameter	Concentration Range
Flow	Intermittent
BOD (mg/l)	40 - 10,000* 1000-4000 [1]
TSS (mg/l)	400 - 2,000
TDS (mg/l)	-
COD (mg/l)	400 - 1500
pH	4 - 11 7.8[2]
Phosphorus (mg/l) (as PO_4)	9 - 210 48[2]
Ammonia Nitrogen (mg/l)	1 - 13 5.5[2]
Total Nitrogen (mg/l)	1 - 115 64[2]
Chloride (mg/l)	45 - 2000* 483[2]
Color	High
Coliform	Present

* See Appendix 5 for parameters which may be inhibitory to biological systems

[1] Narrower range encompassing the majority of plants

[2] Mean for plants reporting

TABLE 8-1-2
DAIRY PRODUCTS

RAW WASTEWATER CHARACTERISTICS BASED UPON

Parameter	Receiving Stations A	Fluid Products B	Cultured Products C	Butter D	Cottage Cheese E	Natural Cheese F	Ice Crea Mix G
Flow Range (gal/1000 lb)[1]	38/224	13/1000	-	150/800	100/1500	25/700	-
Flow Type	B	B	B	B	B	B	B
BOD(kg/kkg)[2]	.02/1.13	.14/17	-	.2/2.0	1.3/42	.24/4.0	.65
TSS(kg/kkg)	-	.13/3.36	-	-	-	.1/0.27	-

1 gallons/1000 lb. milk equivalent (lower limit/upper limit)

2 kg/1000 kg of milk equivalent (lower limit/upper limit)

B Batch Process

5. Control and Treatment Technology

In-Plant Control - Wastewater discharges can be reduced by:

a. Improved management control including measures to minimize product losses, maintain equipment, develop alternative uses for wasted products, and carefully supervise the operation.

b. Engineering improvements to plant, equipment, processes, and ancillary systems can improve production efficiency and reduce waste loads.

Treatment Technology - The standard practice for reducing BOD in this industry has been biological treatment, including activated sludge, aerated lagoons, trickling filters and stabilization ponds.

In addition, land application of wastewater can be practiced by small dairy operations in rural locations. For the treatment systems listed above, equalization is frequently required to prevent shock loads to the system.

Treatment of wastes from the production of whey is more difficult than the other products and can cause upsets in the treatment system. However, the equalization of pollutant loading can reduce the impact of these wastes on biological treatment processes. Whey treatment methods include:

1. Direct return to farmers supplying the milk as feed.
2. Spray irrigation
3. Concentrating and drying

In general, dairy wastes are amenable to biological, as well as chemical treatment if equalization and neutralization are provided as pretreatment. However, care should be exercised in regard to the discharge of whey POTW's. Whey generally has a relatively high BOD5 value, and is normally nitrogen deficient. Consequently, nutrient supplements such as digester supernatent can be helpful in treating the waste in a biological system.

1. General Industry Description

The grain mill industry converts harvested grain and/or grain processing products into food and food intermediary products for human and animal consumption. Starch for consumption as well as for industrial use is also produced. The raw materials include grains such as corn, wheat, rice; and meals such as soybean and bonemeal.

This industrial category includes Standard Industrial Classifications (SIC) 2041, 2043, 2044, 2046 and 2048. This report includes wet milling of corn, but sorghum grain (milo) is excluded. Starch from corn and wheat are included - other vegetable sources are excluded (potato). Establishments engaged in manufacturing prepared dry foods, feed ingredients and adjuncts for animal feed are included. Canned and frozen food preparations are excluded.

2. Industrial Categorization

Subcategory	Designation
Corn Wet Milling	A
Corn Dry Milling	B
Wheat Milling	C
Bulgur Milling	D
Rice Milling	E
Parboiled Rice	F
Animal Feed Manufacturing	G
Hot Cereal Manufacturing	H
Ready-to-Eat Cereal Manufacturing	I
Wheat Starch and Gluten Manufacturing	J

3. Process Description

Grain Mills - Figure 8-2-1 is a flow diagram for the grain industry which shows the processes described below.

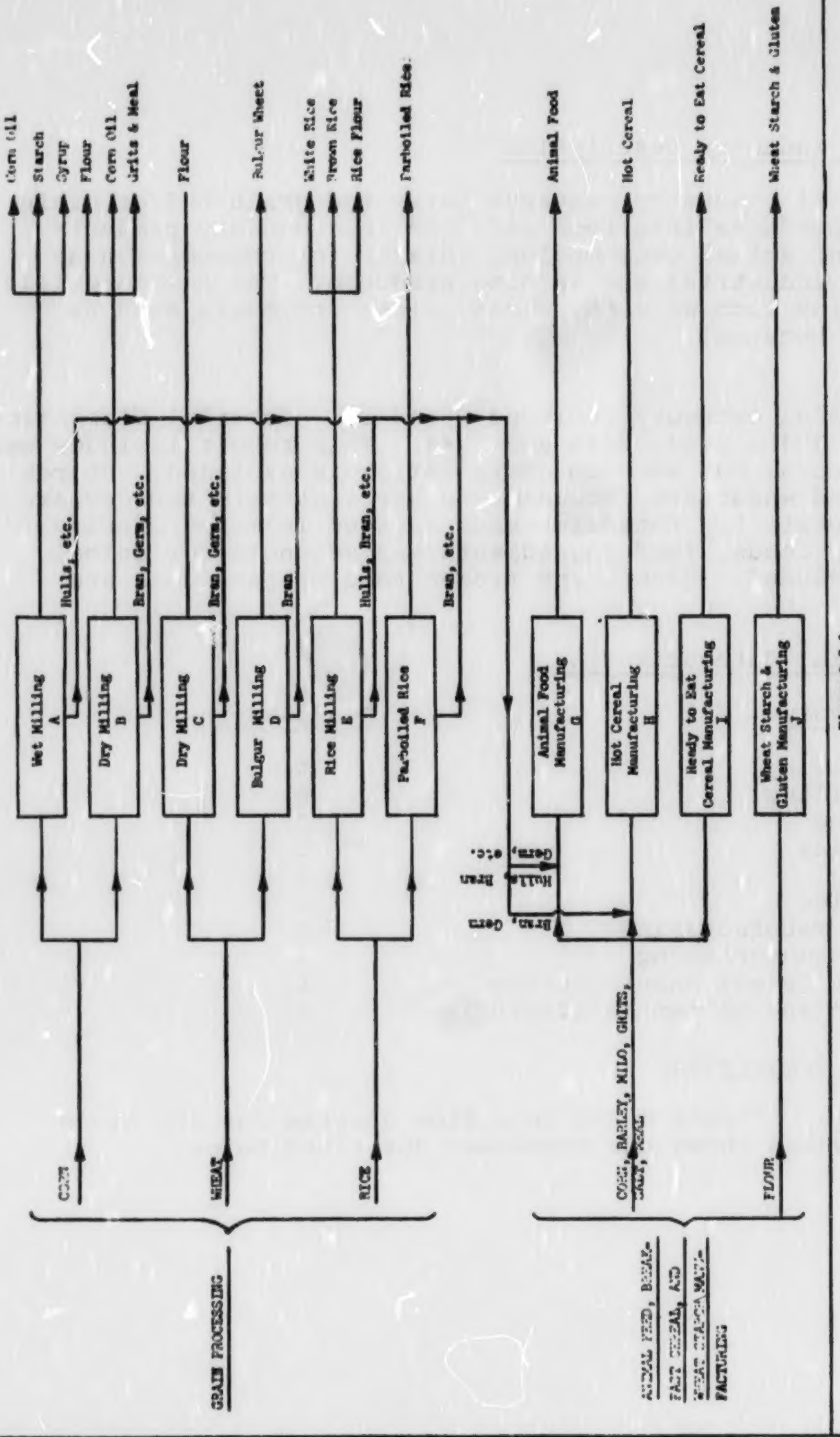
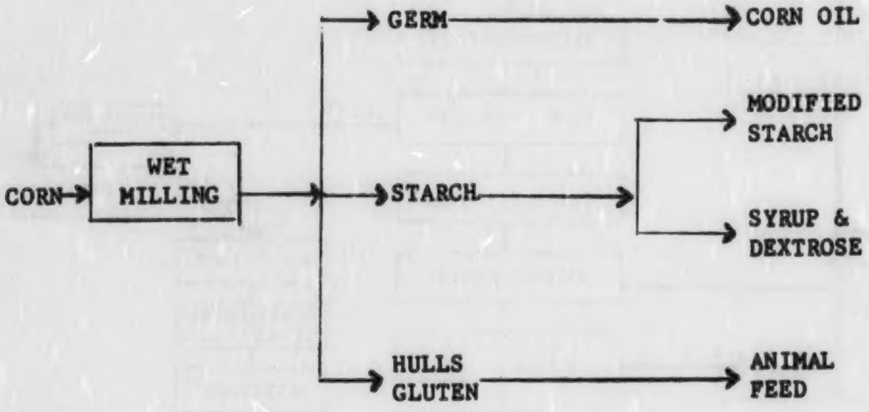

GRAIN PROCESSING
CORN
WHEAT
RICE
Wet Milling A
Dry Milling B
Dry Milling C
Bulgur Milling D
Rice Milling E
Parboiled Rice F
Hulls, etc.
Bran, Germ, etc.
Bran, Germ, etc.
Bran
Hulls, Bran, etc.
Bran, etc.
Corn Oil
Starch
Syrup
Flour
Corn Oil
Grits & Meal
Flour
Bulgur Wheat
White Rice
Brown Rice
Rice Flour
Parboiled Rice
ANIMAL FEED, BREAKFAST CEREAL, AND WHEAT STARCH MANUFACTURING
CORN, BARLEY, MILO, GRITS, OATS, MEAL
FLOUR
Bran, Germ
Hulls, Bran
Germ, etc.
Animal Food Manufacturing G
Hot Cereal Manufacturing H
Ready to Eat Cereal Manufacturing I
Wheat Starch & Gluten Manufacturing J
Animal Food
Hot Cereal
Ready to Eat Cereal
Wheat Starch & Gluten

Figure 8-2-1
GRAIN MILLS
PRODUCT MANUFACTURING FLOW DIAGRAM

Corn Wet Milling (A) - This operation produces starch, oil, syrup, and dextrose, as well as animal feed by-products from whole kernel corn. The corn wet milling operation can be considered to consist of three basic processes:

1. Milling
2. Starch Production
3. Syrup Manufacturing



CORN WET MILLING (A)

Figure 8-2-2

The initial wet milling sequence separates the basic components of the corn kernel into starch, germ, gluten and hulls, from which the end products are derived. The starch slurry may either be dried, modified and then dried or converted into corn syrup or dextrose. In processing the starch slurry, the fractions are apportioned between starch finishing and sweeteners according to market demand. Modification of the starch imparts characteristics to it which may be required for its end use - either for paper or food products, textile manufacturing, building materials, laundries, etc.

Corn wet milling, shown in Figure 8-2-3 begins with the storage and dry cleaning of shelled corn. The corn is steeped in hot sulfurous acid solution in order to soften the kernel for milling. Steeping helps break down the protein holding the starch

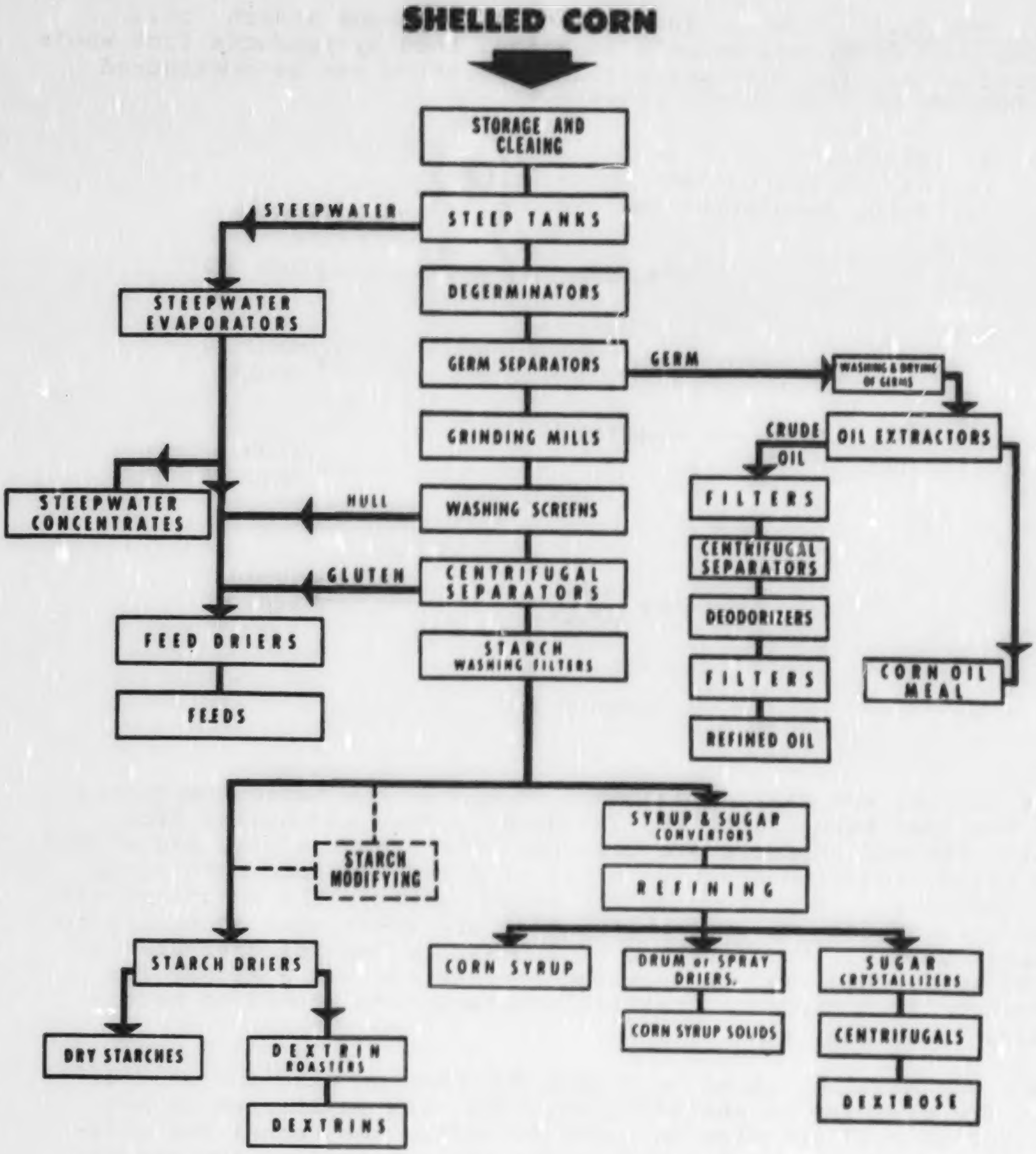

SHELLED CORN
STORAGE AND CLEAING
STEEP TANKS
STEEPWATER
STEEPWATER EVAPORATORS
DEGERMINATORS
GERM SEPARATORS
GERM
WASHING & DRYING OF GERMS
OIL EXTRACTORS
CRUDE OIL
GRINDING MILLS
STEEPWATER CONCENTRATES
HULL
WASHING SCREENS
FILTERS
CENTRIFUGAL SEPARATORS
GLUTEN
CENTRIFUGAL SEPARATORS
DEODORIZERS
FEED DRIERS
STARCH WASHING FILTERS
FILTERS
CORN OIL MEAL
FEEDS
REFINED OIL
SYRUP & SUGAR CONVERTORS
STARCH MODIFYING
REFINING
STARCH DRIERS
CORN SYRUP
DRUM or SPRAY DRIERS.
SUGAR CRYSTALLIZERS
CORN SYRUP SOLIDS
DRY STARCHES
DEXTRIN ROASTERS
CENTRIFUGALS
DEXTRINS
DEXTROSE

FIGURE 8-2-3
THE CORN WET MILLING PROCESS (A)

particles, and removes certain soluble constituents. Part of this steepwater is drained, evaporated, and protein is recovered for addition to animal feeds or for use as a nutrient in fermentation processes. The steeped corn then passes through degerminating mills which tear the kernel apart to free the germ and some starch and gluten. The germ is then separated from the mixture, is washed, dried, and the oil is extracted to produce corn oil. The spent germ is then sold as corn oil meal. Wastewaters from corn wet mills contain large amounts of BOD and suspended solids.

The product slurry passes through a series of washing, grinding and screening operations to separate the starch and gluten from the fibrous material. The hulls are discharged to the feed house for use in animal feeds.

At this point, the main product stream contains starch, gluten, and soluble organic materials. The lower density gluten is then separated from the starch by centrifugation and is processed for animal feed.

The starch slurry can now be directed into one of three basic finishing operations:

1. Ordinary Dry Starch
2. Modified Starches
3. Corn Syrup and Sugar

Starch may be dried and packaged or modified for special uses. Syrups and Sugar-Syrups and sugars are formed by hydrolyzing the starch; partial hydrolysis producing corn syrup, and complete hydrolysis resulting in corn sugar. This step can be accomplished by using mineral acids or enzymes, or a combination of both. The product is then refined and concentrated before storage and shipping. The production of dextrose is quite similar to that of corn syrup.

Corn Dry Milling (B) - Corn is dry cleaned, and then sometimes washed. Wastewaters from washing operations normally go through mechanical solids recovery and then are discharged. The next operation is tempering, or adding water to the corn to raise the moisture content in order to make it more suitable for subsequent milling. Only enough water is added in this operation to reach the desired moisture content and no wastewater is generated. The corn is passed through a series of roller mills, sifters, and separators, where germ and hulls are separated and the fine product stream goes to reduction mills to produce corn flour. Other than infrequent equipment washing, the only process wastewater in this process is that originating from the washing of corn. It is characterized by high BOD and suspended solids. A process flow diagram is shown in Figure 8-2-4.

Wheat Milling (C) - The wheat milling process, presented in Figure 8-2-4 starts with dry, matured, partly cleaned wheat seed. The normal milling of wheat into flour uses water only in tempering (described in (B)) a consumptive process, and in cooling. A few flour mills do wash the wheat, but the vast majority use dry cleaning techniques. The wheat is then ground into flour and its by-products which are used as animal feed additives.

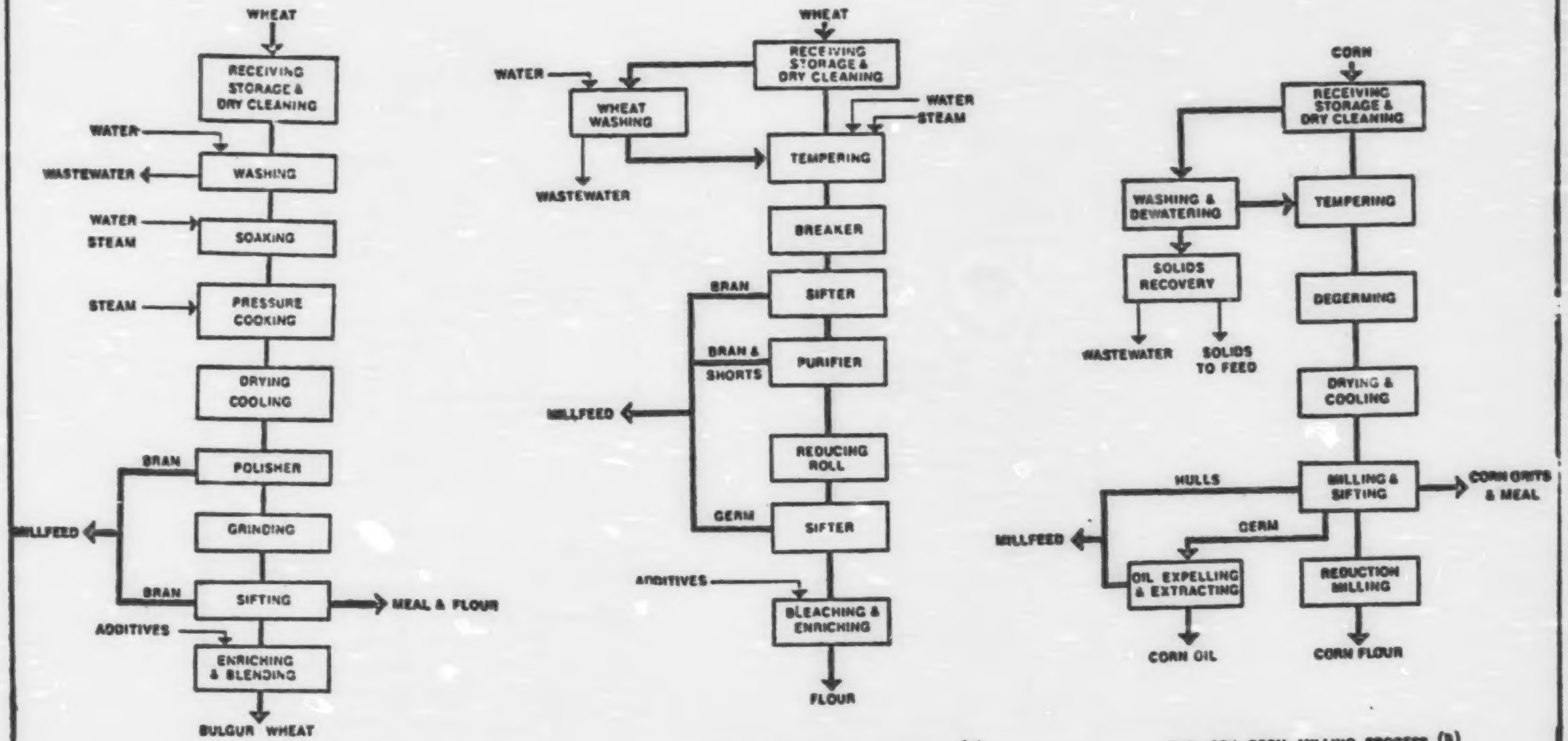
Bulgur Milling (D) - Bulgur is wheat that is parboiled, dried, and partially debranned for use in either cracked or whole grain form. After the washing and the tempering operation (described in (B)), water and live steam are added to the grain and it is cooked, then dried. The dried wheat is then polished, ground and sifted. The bulgur is packaged, and the by-products are used as animal feed additives. Wastewaters are high in BOD, COD, and suspended solids. A process flow diagram is shown in Figure 8-2-4.

Rice Milling (E) - Rough rice is cleaned and mechanically processed to separate bran, shells, hulls from the brown rice, white rice, and rice flour. The operation utilizes no process waters and, hence, generates no wastewaters. A process flow diagram is shown in Figure 8-2-5.

Parboiled Rice (F) - Rice that has been sorted and cleaned is cooked under pressure, then dried. Modest amounts of wastewaters high in BOD are generated. A process flow diagram is shown in Figure 8-2-5.

Animal Feed Manufacturing (G) - The processing of various grains, grain milling by-products, and other materials into prepared animal feed requires only small volumes of process water. Wastewaters include boiler blowdown and cooling waters. No process wastewaters are discharged.

Hot Cereal Manufacturing (H) - In general, only dry milling and blending operations are involved in hot cereals manufacture. Water is consumed in several processes, but no wastewaters result from this operation.


WHEAT
RECEIVING STORAGE & DRY CLEANING
WATER
WASHING
WASTEWATER
WATER
STEAM
SOAKING
STEAM
PRESSURE COOKING
DRYING COOLING
BRAN
POLISHER
MILLFEED
GRINDING
BRAN
SIFTING
MEAL & FLOUR
ADDITIVES
ENRICHING & BLENDING
BULGUR WHEAT
WHEAT
RECEIVING STORAGE & DRY CLEANING
WATER
WHEAT WASHING
WASTEWATER
WATER
STEAM
TEMPERING
BREAKER
BRAN
SIFTER
BRAN & SHORTS
PURIFIER
MILLFEED
REDUCING ROLL
GERM
SIFTER
ADDITIVES
BLEACHING & ENRICHING
FLOUR
CORN
RECEIVING STORAGE & DRY CLEANING
WASHING & DEWATERING
TEMPERING
SOLIDS RECOVERY
WASTEWATER
SOLIDS TO FEED
DEGERMING
DRYING & COOLING
HULLS
MILLING & SIFTING
CORN GRITS & MEAL
MILLFEED
GERM
OIL EXPELLING & EXTRACTING
REDUCTION MILLING
CORN OIL
CORN FLOUR

THE BULGUR PROCESS (D)

THE WHEAT MILLING PROCESS (C)

THE DRY CORN MILLING PROCESS (B)

FIGURE 8-2-4
GRAIN MILLING

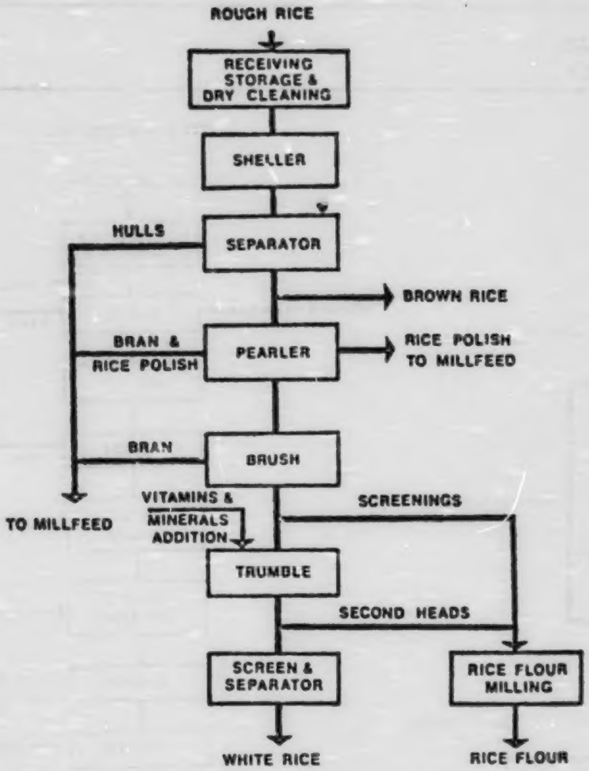

ROUGH RICE
RECEIVING STORAGE & DRY CLEANING
SHELLER
SEPARATOR
HULLS
BROWN RICE
PEARLER
BRAN & RICE POLISH
RICE POLISH TO MILLFEED
BRUSH
BRAN
TO MILLFEED
VITAMINS & MINERALS ADDITION
SCREENINGS
TRUMBLE
SECOND HEADS
SCREEN & SEPARATOR
RICE FLOUR MILLING
WHITE RICE
RICE FLOUR

FIGURE 5
THE RICE MILLING PROCESS (E)

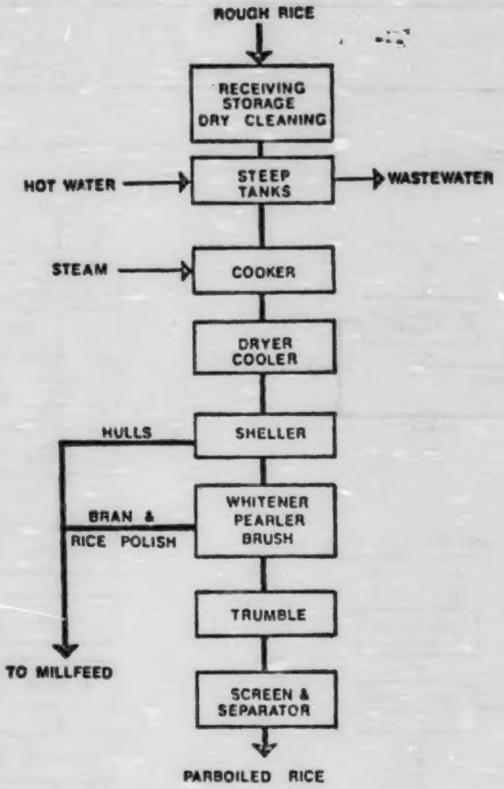

ROUGH RICE
RECEIVING STORAGE DRY CLEANING
HOT WATER
STEEP TANKS
WASTEWATER
STEAM
COOKER
DRYER COOLER
SHELLER
HULLS
WHITENER PEARLER BRUSH
BRAN & RICE POLISH
TRUMBLE
TO MILLFEED
SCREEN & SEPARATOR
PARBOILED RICE

FIGURE 6
THE PARBOILED RICE PROCESS (F)

FIGURE 8-2-5

RICE MILLING

Ready-To-Eat Cereal Manufacturing (I) - Ready-to-eat cereals include flaked, crisped, shredded, puffed and extruded varieties. A large portion of the total water consumption of a plant is due to wet clean-up and washing operations, but several of the processing steps also require water. Except for the cooking operation in shredded cereal manufacture, the added moisture remains with the product until it is released as a vapor in a drying operation or it is consumed. Wastewaters from shredded cereal manufacturing are higher in BOD, COD, dissolved and suspended solids than the other ready-to-eat cereals. Water is used for cooling equipment and in wet scrubbers for air pollution control. A process flow diagram for shredded cereal production is shown in Figure 8-2-6.

Wheat Starch and Gluten Manufacturing (J) - Lower grades of wheat flour are mixed with water into a dough, allowed to mature, and after repeated washings are separated into starch and gluten. The gluten, high in protein, is dried and packed and used as an ingredient in bakery produce. It can also be processed into monosodium glutamate (MSG), a flavor enhancer. The starch-laden stream is thickened, dewatered, dried and packaged. Wheat starch has widespread use in the food and textile industries and in adhesives. Moderate amounts of wastewaters are generated which are high in BOD and suspended solids. A process flow diagram is shown on Figure 8-2-7.

4. Wastewater Characterization

Wastewater generated in grain mills may be somewhat deficient in nitrogen for biological waste treatment. Wet corn mills typically generate large volumes of wastes containing significant quantities of BOD_5 and suspended solids. These concentrations in turn depend to a large degree on the quantities of once-through contact cooling waters utilized in the process. Wastewaters from ready-to-eat cereal plants vary considerably in quantity and character.

Tables 8-2-1 and 8-2-2 contain raw wastewater data for the various subcategories.

5. Control and Treatment Technology

In the Grain Processing category only Corn Wet Milling (A) has had attention focused on control and treatment of its wastes. This is due to the large quantities of wastewaters discharged in contrast to the much smaller amounts generated by the other types of grain milling (B, C, D, E, F). In many instances, the treatment technologies developed for Corn Wet Milling (A) can be applied to other subcategories.

Animal Feed (G) and Hot Cereal (H) generate no process wastewaters. Most of the Ready-To-Eat Cereals (I) industry discharge medium strength wastes to large municipal systems which are capable of handling the industrial waste loads. Some plants

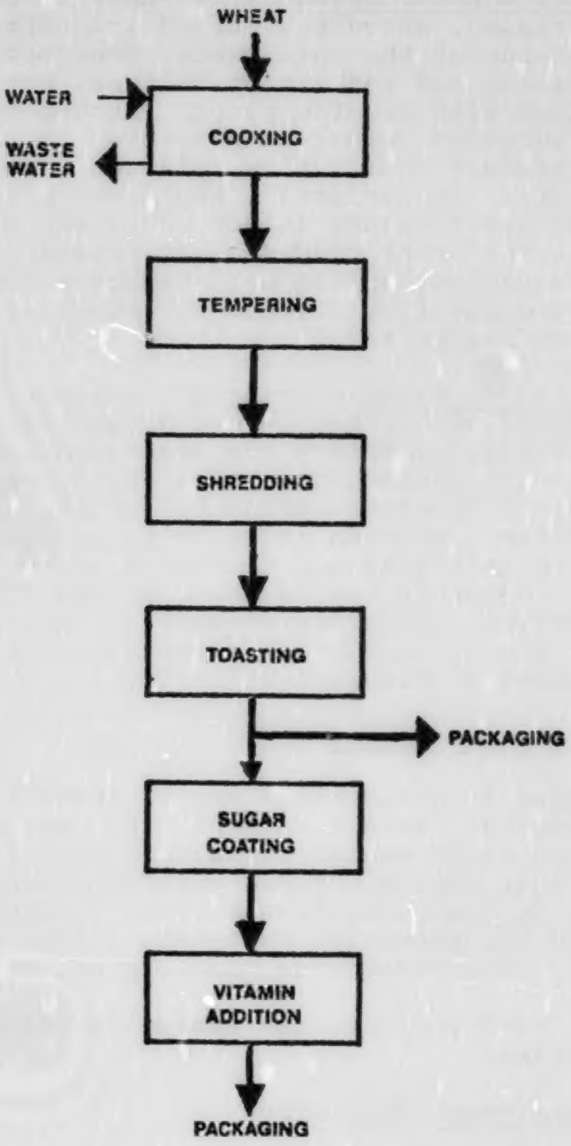

WHEAT
WATER
COOKING
WASTE WATER
TEMPERING
SHREDDING
TOASTING
PACKAGING
SUGAR COATING
VITAMIN ADDITION
PACKAGING

FIGURE 8-2-6

SHREDDED CEREAL PRODUCTION (I)

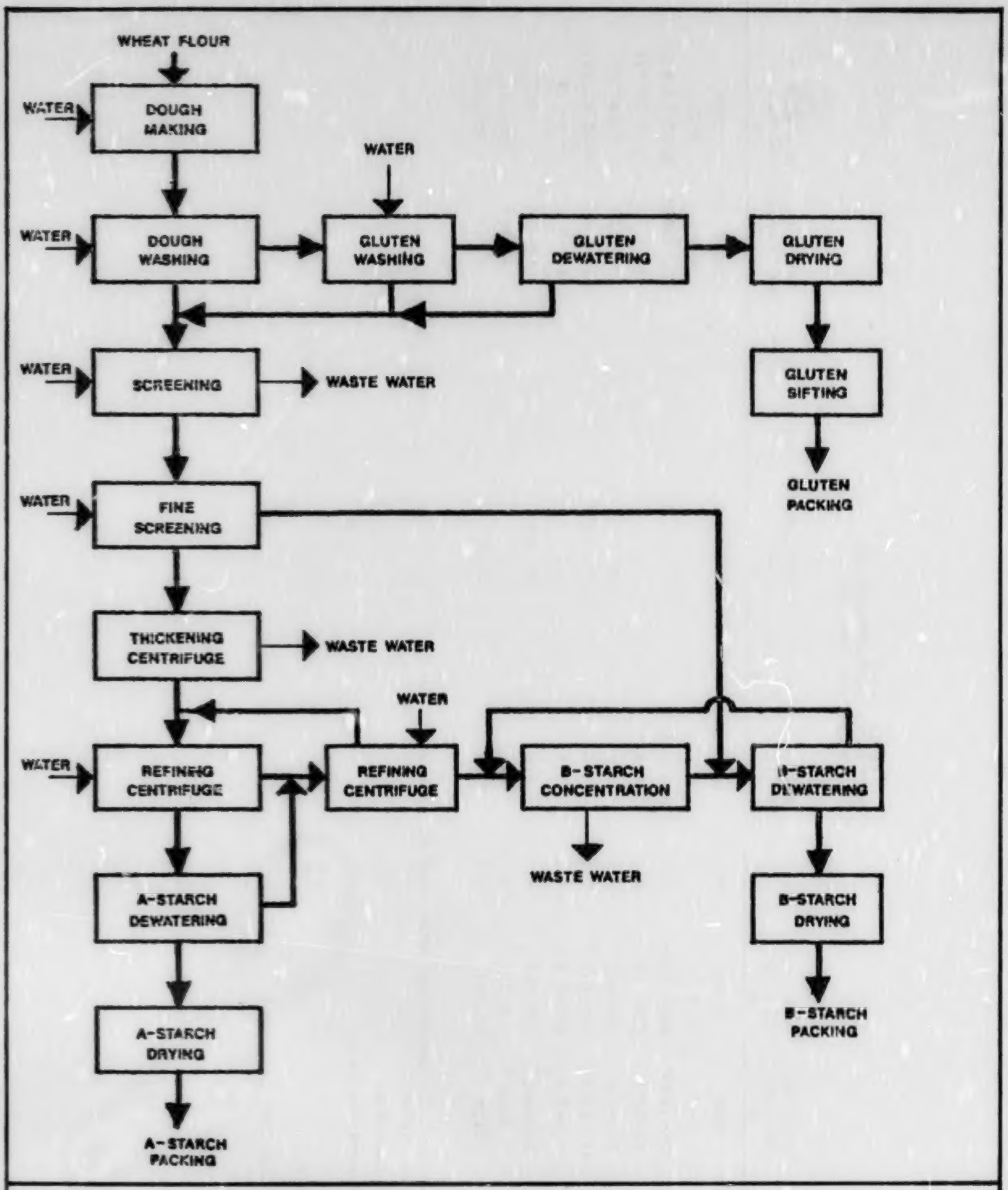

WHEAT FLOUR
WATER
DOUGH MAKING
WATER
WATER
DOUGH WASHING
GLUTEN WASHING
GLUTEN DEWATERING
GLUTEN DRYING
WATER
SCREENING
WASTE WATER
GLUTEN SIFTING
GLUTEN PACKING
WATER
FINE SCREENING
THICKENING CENTRIFUGE
WASTE WATER
WATER
WATER
REFINING CENTRIFUGE
REFINING CENTRIFUGE
B-STARCH CONCENTRATION
B-STARCH DEWATERING
WASTE WATER
A-STARCH DEWATERING
B-STARCH DRYING
B-STARCH PACKING
A-STARCH DRYING
A-STARCH PACKING

FIGURE 8-2-7

WHEAT STARCH AND GLUTEN MANUFACTURING (J)

TABLE 8-2-1
RAW WASTEWATER CHARACTERISTICS
GRAIN PROCESSING INDUSTRY

Parameter, mg/l	Corn Wet Milling A	Corn Dry Milling B	Wheat Milling C	Bulgur Milling D	Rice Milling E	Parboiled Rice F	Animal Feed G	Hot Cereal H	Ready to Eat Cereal I	Starch & Gluten J
Average Flow (MGD)	25MM	130M	Nil	10M-30M	0	70M-200M	0	0	140M-8.4MM	120M
Flow Type	B-C	B		B		B			B-C	B-C
BOD_5	225-7600*	600-2748*	Nil	238-521		1280-1305*			420-2500*	6200-14,633*
TSS	81-2458	1038-3485	Nil	294-414		33-77			80-1572	4176-14,824
TDS	Present	Present	Nil	Present		1687			0-7619	Present
COD	473-4560*	1795-4901*	Nil	800		2810-3271*			804-6040*	9300-25,040*
pH	5.9-7.9	3.7-7.8	Nil	5.8		6-9			4.1-8.6	3.5-4.9
Phosphorus	Present[1]	30-65*	Nil	5.6		30-65*			Present[1]	100
Nitrogen	0-10[1]	0-10	0-10	0-10		7.0			5-30[1]	350-400
Temperature (^{o}C)	High	Normal	Nil	High		High			71-74*	Normal

Note: *See Appendix 5 for parameters which may be inhibitory to biological systems.

B - Batch Operation

C - Continuous Operation

M - 1000

MM - 1,000,000

[1] May be nutrient deficient

GRAIN PROCESSING

RAW WASTEWATER DATA
BASED UPON PRODUCTION
TABLE 8-2-2

Parameter	A Corn Wet Milling	B Corn Dry Milling	C Wheat Milling	D Bulgur	E Rice	F Parboiled Rice	G Animal Feed	H Hot Cereal	I Ready to Eat Cereal	J Wheat, Starch & Gluten
Flow Range (1/kkg)^1	3.1M/41.7M	480/900	Neg.	38M/115M	0	1.4M/2.1M	0	0	2.5M/9.6M	7.4M/12.4M
Average Flow (1/kkg)	18.3M	-	Neg.	-	0	-	0	0	5.82M	9.95M
BOD Range (kg/kkg^2)	2.1/12.5	-	Neg.	-	0	-	0	0	2.2/18.2	80/108
BOD Avg. (kg/kkg)	7.4	1.14	Neg.	.11	0	1.8	0	0	6.6	90.7
Suspended Solids range (kg/kkg)	.5/9.8	-	Neg.	-	0	-	0	0	.6/2.7	52/110
Suspended Solids Avg. (kg/kkg)	3.8	1.62	Neg.	.10	0	.07	0	0	1.4	75.7
COD Range (kg/kkg)	6.8/22.3	-	Neg.	-	0	-	0	0	5.7/42.4	116/260
COD Avg. (kg/kkg)	14.8	-	Neg.	-	0	-	0	0	15.7	198.6

Note: 1 1/kkg liters/1000 kg product produced (lower limit/upper limit)
2 kg/kkg kilograms/1000 kg product produced (lower limit/upper limit)
Neg. Negligible
- Concentration Unknown
M - 1000
MM - 1,000,000

provide pretreatment facilities to reduce waste loadings prior to municipal discharge. Both in-plant control measures and effluent treatment systems are essential to wastewater reduction.

In-Plant Controls - All corn wet mills presently incorporate many water recycling and reuse techniques. Through research, new markets were found for materials that were once wasted, such as steepwater. Efforts to improve product recovery and simultaneously to reduce waste discharges, have led to innovative process operations which utilize recycled water.

Several plants have converted barometric condensers to surface condensers to reduce wastewater volumes. Other plants recirculate the barometric cooling water over cooling towers.

Improved operator control and expanded evaporator capacity can reduce liquor boil-over and resultant heavy discharges. General operational and housekeeping procedures have a marked effect on the amount of wastes discharged.

It is doubtful that any major reductions in waste load can be achieved through in-plant controls or modifications at existing starch plants (J). Since product yield is economically crucial to these producers, a high degree of product recovery is practiced. New plants are being designed to further reduce wastewater discharges.

Treatment Processes - Several Wet Corn Mill (A) plants provide treatment or pretreatment of the plant effluent. Treatment and pretreatment processes range from settling and/or aeration to complete activated sludge systems. Frequent upsets in this industry cause shock loads which reduce treatment efficiency.

The other Grain Milling processes (B, C, D, E, F) generate wastewaters that are amenable to conventional biological treatment.

Process wastewater from wheat starch and gluten (J) manufacturing is readily biodegradable and treatable by conventional biological treatment systems. Pilot plant studies on one pretreatment facility yielded BOD reductions of up to 98%. The system included aeration and settling, rotating biological disc, and a polishing pond.

Wastewater treatment practices are shown on Table 8-2-3.

Table 8-2-3

GRAIN INDUSTRY
Wastewater Treatment Practices
Percent Reduction

Treatment Method	Corn Wet Milling A	Corn Dry Milling B	Bulgur D	Parboil Rice E	Ready-To-Eat I	Starch & Gluten J
Activated Sludge						
BOD reduction	80		92.5	92.8	92	95.6-97.8
SS reduction	58		91.7		59	94.7-98.7
Equalization + Act. Sludge						
BOD reduction	90				94	96.7-98.3
SS reduction	80				69	96.0-98.7
Equalization + Act. Sludge + Stabilization Lagoon						
BOD reduction	95				95-97.5	98.3-98.9
SS reduction	90				75-87	98-99
Equalization + Act. Sludge + Deep Bed Filtration						
BOD reduction	97.4				97.4-98.3	99.4-99.7
SS reduction	96.9				91.4-95.7	99.6-99.7
Equalization + Act. Sludge + Deep Bed Filtration + Activated Carbon Filtration						
BOD reduction	99.5				99.6	99.8-99.9
SS reduction	99.0				97.9	99.8-99.9
Equalization + Act. Sludge + Deep Bed Filt. + Act. Carbon Filt., + Reverse Osmosis						
BOD reduction	99.5				99.6	99.9
SS reduction	99.0				97.9	99.9
Primary Sedimentation						
BOD reduction		43				
SS reduction		80				
Primary Sedimentation + Activated Sludge						
BOD reduction		94.3				
SS reduction		96.0				
Primary Sedimentation + Act. Sludge + Stabilization Lagoon						
BOD reduction		97.4				
SS reduction		98.2				
Prim. Sedimentation + Act. Sludge + Deep Bed Filtration						
BOD reduction		98.6				
SS reduction		99.4				
Prim. Sed., + Act. Sludge + Deep Bed Filt., Activated Carbon Filt.						
BOD reduction		99.7				
SS reduction		99.8				
Act. Sludge + Deep Bed Filt.						
BOD reduction			96.2	98.2		
SS reduction			97.8	86.4		
Act. Sludge, Deep Bed Filt. + Activated Carbon Filt.						
BOD reduction			98.8	99.6		
SS reduction			98.6	90.9		
Activated Sludge + Stabilization Lagoon						
BOD reduction				96.7		

1. General Industry Description

The processes of the canned and preserved fruits and vegetables industry extend the shelf life of raw commodities through the use of various preservation methods including canning, freezing, dehydrating, and brining. Fruit and vegetable preservation generally includes the following unit operations: cleaning and sorting, peeling, sizing, stabilizing and processing.

Fruit and vegetable processing plants are major water users and waste generators. Raw foods must be rendered clean and wholesome and food processing plants must be sanitary at all times.

For the most part these wastes have been shown to be biodegradable, although salt is not generally removed during the treatment of olive storage and processing brines, cherry brines, and sauerkraut brines.

This industry encompasses Standard Industrial Classifications (SIC) 2032, 2033, 2034, 2035, 2037, and 2099.

2. Industrial Categorization

The apple, citrus and potato processing segment of the industry has been subcategorized as follows:

Subcategory	Designation
Apple Juice	A
Apple Products	B
Citrus Products	C
Frozen Potato Products	D
Dehydrated Potato Products	E

The above subcategorization does not include caustic peeled and dehydrated apple products, and pectin and pharmaceuticals derived from citrus products. The remaining part of the industry has been tentatively subcategorized, but is still subject to change. The tentative subcategorization is as follows:

1. Added ingredients
2. Apricots
3. Asparagus
4. Baby foods
5. Beets
6. Broccoli
7. Brussels sprouts
8. Caneberries, blueberries
9. Carrots
10. Cauliflower
11. Cherries, sweet and sour

12. Cherries, brined
13. Corn
14. Corn chips
15. Cranberries
16. Dehydrated onions and garlic
17. Dehydrated vegetables
18. Dried fruits, prunes, figs
19. Dry beans, canned
20. Ethnic vegetables, Chinese and Mexican
21. Grape pressing
22. Grape juice
23. Jams, jellies and preserves
24. Lima beans
25. Mayonnaise and salad dressings
26. Mushrooms
27. Olives
28. Onions (canned)
29. Peaches
30. Pears
31. Peas
32. Pickles, fresh pack
33. Pickles, process pack
34. Pimentos
35. Pineapples
36. Plums
37. Potato chips
38. Prune juice
39. Pumpkin and squash
40. Raisins
41. Sauerkraut, cutting
42. Sauerkraut, canning
43. Snap beans (green and wax)
44. Soups
45. Spinach/leafy greens
46. Strawberries
47. Sweet potatoes
48. Tomatoes, peeled
49. Tomato products
50. Tomato - starch - cheese, canned specialities
51. White potatoes, whole

3. Process Description

In general, all subcategories have similar process operations as follows:

Field to Plant - The crop is harvested, separated from "trash" (stems, leaves), sorted, transported, and received at the plant. No wastewaters are generated.

Washing and Rinsing

Prior to processing the fruits and vegetables are washed and rinsed by means of flumes, soak tanks, water sprays, flotation chambers, or any combination of these methods. Great quantities of water are used. Detergents and ultrasonic techniques are also being tested for increased cleaning efficiency.

Sorting (Grading)

The commodity is sorted and graded by mechanical,optical,manual or hydraulic means. Density graders employing brine of controlled density are used to separate mature from over mature produce. Weed seeds, chaff, and stones may be separated by density and in froth separators.

Stemming, Snipping, Trimming

Stemming, snipping, and trimming are accomplished by a variety of mechanical means. No wastewaters are generated.

In-Plant Transport

Various means have been adapted for conveying fruit or vegetable products at unloading docks into and through the processing plant. These include fluming, elevating, vibrating, screw conveying, air propulsion, negative air conveying, hydraulic flow, and jet or air blasting. Water, in one way or another, has been extensively used in conveying products within plants because it has been economical in such use and because it serves not only as conveyance but also for washing and cooling.

It has been traditional to consider water an economical means to transport fruits and vegetables within a plant and to assume there was some sanitary significance to such use, not only for the product, but also for the equipment. A significant disadvantage, however, may be leaching of solubles from the product, such as sugars and acids from cut fruit; and sugars and starch from cut corn, beets, and carrots. Alternative systems to decrease such losses from water have been investigated, such as osmotically equivalent fluid systems.

Peeling

Many fruits and vegetables are peeled for processing. This serves the multiple purpose of removing residual soil, pesticide residues, and coarse, fuzzy, or tough peeling with unplesant appearance, mouth feel, or digestive properties.

Peeling is accomplished mechanically by cutting or abrasion; thermally by puffing and loosening the peel by application of steam, hot water, hot oil flame, or blasts of heated air; or chemically, principally using caustic soda (with optional surfactants) to soften the cortex so it may be removed by mechanical scrubbers or high-pressure water sprays.

Pitting, Coring, Slicing and Dicing

Pitting, coring, slicing and dicing are accomplished by a variety of mechanical techniques depending upon commodity used and end product desired. No wastewaters are generated.

Pureeing and Juicing

Widely varied techniques are used for pressing and separating fluid from fruits and vegetables. Equipment includes reamers and a wide variety of crusher-presses, either batch or continuous in operation.

The oxygen and other gases (nitrogen, carbon dioxide) present in freshly pressed or extracted fruit and vegetable juices may be effectively removed by deaeration under vacuum. The liquids to be deaerated are pumped into an evacuated chamber either as a spray or as a thin film. Modern deaerators operate at a vacuum of 29 inches or above. Deaeration properly carried out not only improves color and flavor retention, but reduces foaming during filling and also reduces separation of suspended solids.

In the concentration of solutions by evaporation, the liquid to be concentrated continuously flows across a heat exchange surface which separates it from the heating medium. There are various types of evaporators, including: open kettles, shell-and-tube heat exchangers, flash evaporators, rising and falling film evaporators, plate type evaporators, thin-film centrifugal evaporators, vapor separators, vacuum evaporators and heat pump evaporators.

The process involves heating the product to evaporation and separating the vapors from the residual liquid.

Size Reduction

A wide range of size reduction equipment is required to produce different types of particulated solids. Selection of a machine which can most economically produce desired results is affected by physical characteristics of the material and by the required particle size and shape.

Blanching

Blanching (scalding or parboiling) of vegetables for canning, freezing,or dehydration is done for one or more reasons: removal of air from tissues; removal of solubles which may affect clarity of brine or liquor; fixation of pigments; inactivation of enzymes; protection of flavor; leaching of undesirable flavors or components such as sugars; shrinking of tissues; raising of temperature; and destruction of microorganisms.

Blanching is accomplished by putting the products in contact with water or steam. In almost all cases for preparation of vegetables to be frozen, it is imperative that the blancher processes be terminated quickly. Consequently, some type of cooling treatment is used. Typically, if the product has been water blanched, the vegetable is passed over a dewatering screen and cooled either by cold water flumes or cold water sprays. Product to be canned is usually not cooled after blanching.

The pollution loads from blanching are a significant portion of the total pollution load in the effluent stream during the processing of certain vegetables.

Canning

The sanitary codes of most states require that cans be washed before being filled. There are usually three steps in the can cleaning operation. First, the cans travel a short distance in the inverted position; second, they are flushed with a relatively large volume of water under high pressure; and third, they travel another short distance in the inverted position for the purpose of draining excess water. This is usually accomplished mechanically.

The commodity is then filled into the can by hand, semiautomatic machines, or fully automatic machines, depending on the product involved. In some products, there is a mixture of product and brine or syrup. In other cases, brine or syrup is added hot or cold as top-off liquid. When the top-off is cold, it is necessary to exhaust the headspace gases to achieve a vacuum and maintain product quality.

Exhausting in order to create a vacuum, is usually accomplished by one of the three methods:

1. Thermal exhaust or hot filling. The contents of the container are heated to a temperature of 160° to 180°F, prior to closing the container. Contraction of the contents of the container after sealing produces a vacuum.

2. Mechanical. A portion of the air in the container headspace is pumped out by a gas pump.

3. Steam displacement. Steam is injected into the headspace to replace the air, and sealed. A vacuum is produced when the steam condenses.

Drying or Dehydration

Continuous belt dryers are the most commonly used method for dehydration. They are usually long and multi-staged with baffled chambers which blow heated and sometimes desiccated air from over and under the bed-depth of the raw slices. Residence time in this type of dryer is usually ten to twenty hours, resulting in a product that has a finished moisture content of no greater than 4.25 percent of onions or 6.0 per cent for garlic.

Post-Drying Operations

After dehydration the dried slices are usually screened, milled, aspirated, separated, and ground in various mechanical combinations to achieve the final desired piece size.

Mixing and Cooking

Certain commodities utilize additional ingredients in the manufacture of the finished products. For example, many frozen vegetables are prepared with butter, cheese, cream sauce, sugar, starch and tomato sauce added. Equipment washouts and spills add an incremental waste load to the total plant waste production.

Freezing

Freezing is accomplished in a tunnel frezzer. The frozen commodity is then inspected, sorted and sized prior to packing.

The only waste loads generated from this operation are from the clean-up operations and from cooling water.

Clean-Up

Clean-up operations vary widely from plant to plant and from product to product. Normally the plant and equipment is cleaned at the end of the shift, usually by washing down the equipment and floors with water. In some plants it is desirable to maintain a continuous cleaning policy so that end-of-shift clean-up is minimized.

Clean-up begins with a dry collection of wastes followed by a washdown. The washdown may be done with either water alone or with water mixed with detergent. Water is applied through either high-volume, low-pressure hoses or low-volume, high-pressure hoses.

In some operations, such as the mayonnaise processing operation, clean water is used to flush out the entire system at the end of the shift to remove any residues which might harbor bacteriological growth.

The water used in clean-up operations generally flows through drains directly into the wastewater system.

4. Wastewater Characterization

Wide ranges of wastewater volume and organic strength are generated by this industry depending upon the particular commodity being processed, the particular operation employed, and daily and seasonal variations. Treatment facilities must be designed to handle large volumes intermittently. Citrus wastes are highly putrescible and contain pectic substances which interfere with the settling of suspended solids.

Table 8-3-1 gives the raw waste characteristics for this industry. The table has been grouped by the following formula:

Group I - Commodities with BOD less than 500 mg/l
Group II - Commodities with BOD between 500-1000 mg/l
Group III - Commodities with BOD between 1000-2000 mg/l
Group IV - Commodities with BOD between 2000-3000 mg/l
Group V - Commodities with BOD between 3000-5000 mg/l
Group VI - Commodities with BOD greater than 5000 mg/l

5. Control and Treatment Technology

In-Plant Control - The use of field washing in place of certain washing procedures in the processing plant can reduce the waste loads produced at the processing plant. Wastewaters produced in the field can easily be disposed of on land, eliminating a wastewater source. The use of mechanical peel removal in place of water can reduce the waste load.

The use of dry methods of in-plant transport in place of water transport methods has been examined by this industry. Although dry transport methods greatly reduce the waste loads, they are much more costly. The use of fluidized bed and microwave blanching techniques have been examined and have been found to reduce waste loads; however the costs have been found to be too high to be viable at the present time.

In-plant water reuse has been practiced in this industry. An example of this is the use of spent cooling water to wash products following blanching, and then in turn using this water to wash the incoming raw product. In some cases water to be reused will require treatment such as chlorination to meet product quality requirements.

Treatment Technology - As can be seen from Table 8-3-1 the major pollutant parameters generated by this industry are BOD and TSS. Suspended solids can be removed by screening, sedimentation or flocculation with clarification. Since caustic is used in some operations, pH adjustment may be required in some cases.

TABLE 8-3-1
CANNED AND PRESERVED FRUITS AND VEGETABLES INDUSTRY
RAW WASTEWATER CHARACTERISTICS

Group I		Group II		Group III		Group IV		Group V		Group VI	
BOD_5 - Less Than 500 mg/1		BOD_5* 500 - 1000 mg/1		BOD_5* 1000 - 2000 mg/1		BOD_5* 2000 - 3000 mg/1		BOD_5* 3000 - 5000 mg/1		BOD_5* - Greater Than 5000 mg/1	
Subcategory	TSS mg/1	Subcategory	TSS mg/1	Subcategory	TSS mg/1	Subcategory	TSS mg/1	Subcategory	TSS mg/1	Subcategory	TSS mg/1
C Citrus	130	A Apple Juice	104	B Apple Prod.	150	9 Carrots	262-1540	12 Cherries, Brined	87-130	5 Beets	367-4330
3 Asparagus	43-114	1 Added Ingred.		D Frozen Potatoes	1716	11 Cherries(1) Sweet & Sour	48-125	18 Dried Fruits Prunes Figs	8-568	13 Corn	131-2440
6 Broccoli	100-455	4 Baby Foods	101-533	E Dehydrated Potatoes	981	14 Corn Chips	1650	23 Jams, Jellies & Preservatives	404-711	32 Pickles Fresh Pack	42-6130
7 Brussels Sprouts	29-1680	15 Cranberries	35-84	2 Apricots	33-387	21 Grape Press.	90-530	25 Mayonnaise & Salad Dressings	899-1510	40 Raisins	7-5290
8 Caneberries Blueberries	52-184	20 Ethnic Veget. Chin. & Mex.	140-246	19 Dry Beans, Canned	80-393	22 Grape Juice	216-228	30 Pears	84-702	47 Sweet Potatoes	4010-12,200
10 Cauliflower	18-113	24 Lima Beans	82-584	26 Mushrooms	33-467	31 Peas	79-673	35 Pineapples	837-1160	51 White Potatoes Whole	1660-24,300
16 Dehydrated Onions and Garlic	168-778	38 Prune Juice	153-165	28 Onions(Canned)	175-1030	37 Potatoe Chips	1450-3910	39 Pumpkin and Squash	185-1600		
17 Dehydrated Vegetables	304	41 Sauerkraut Cutting	143	29 Peaches	164-1020						
27 Olives (1)	400	46 Strawberries	96-210	33 Pickles Process Pack	83-574						
43 Snap Beans (Green & Wax)	76-348	48 Tomatoes Peeled	280-1280	34 Pimentos	84-119						
44 Soups	365	49 Tomato Products	512-1180	36 Plums	60-187						
45 Spinach/ Leafy Greens	19-419			42 Sauerkraut(1) Canning	213-363						
				50 Tomato - Starch,Cheese, C. SP.	109-715						

Note: Fruit and vegetable wastes may be nitrogen deficient.
*See Appendix 5 for parameters which may be inhibitory to biological systems.
(1)May have high concentration of dissolved solids.

BOD removal is accomplished with sedimentation, activated sludge, aerated lagoons, trickling filters, and anaerobic processes. Some waste streams are nutrient deficient, and require nitrogen and phosphorus addition.

Advanced waste treatment techniques are also applicable to wastes from this industry, such as activated carbon, filtration, and electrodialysis. Table 8-3-2 gives the removal efficiencies for the treatment practices of this industry.

Table 8-3-2
Canned and Preserved Fruits and Vegetables Industry

Wastewater Treatment Practices

Pollutant and Method	Removal Efficiencies Percent
TSS	
Flotation	50-80
Primary Sedimentation	30-75
BOD	
Primary Sedimentation	50-80
Biological Treatment	40-99

1. General Industry Description

The canned and preserved fish and seafood industry, including industrial products, has been expanding steadily from the use of drying and curing techniques to the various technologies involved in preserving, canning, freezing, and rendering of fishery products. There is great variability in the length of processing season and amount of material processed in the industry. There is also a tremendous variability in both the amount of water used and the waste loading from process plant to process plant. In general, wastes from this industry contain BOD, suspended solids, and oil and grease.

This industry includes Standard Industrial Classifications (SIC) 2091 and 2092.

2. Industrial Categorization

The Catfish, Crab, Shrimp and Tuna segment of the Canned and Preserved Seafood Process industry has been subcategorized as follows:

Subcategory	Designation
Farm-raised Catfish Processing	A
Conventional Blue Crab Processing	B
Mechanized Blue Crab Processing	C
Non-Remote Alaskan Crab Meat Processing	D
Remote Alaskan Crab Meat Processing	E
Non-Remote Alaskan Whole Crab & Crab Section Processing	F
Remote Alaskan Whole Crab & Crab Section Processing	G
Dungeness & Tanner Crab Processing in the Contiguous States	H
Non-Remote Alaskan Shrimp Processing	I
Remote Alaskan Shrimp Processing	J
Northern Shrimp Processing in the Contiguous States	K
Southern Non-Breaded Shrimp Processing in the Contiguous States	L
Breaded Shrimp Processing in the Contiguous States	M
Tuna Processing	N

The remaining segment of the industry has been tentatively divided into the following subcategories:

1) Fish meal processing
2) Alaskan hand-butchered salmon processing
3) Alaskan mechanized salmon processing
4) West Coast hand-butchered salmon processing
5) West Coast mechanized salmon processing
6) Alaskan bottom fish processing
7) Non-Alaskan conventional bottom fish processing
8) Non-Alaskan mechanized bottom fish processing
9) Hand-shucked clam processing
10) Mechanized clam processing
11) West Coast hand-shucked oyster processing
12) Atlantic and Gulf Coast hand-shucked oyster processing
13) Steamed/canned oyster processing
14) Sardine processing
15) Alaskan scallop processing
16) Non-Alaskan scallop processing
17) Alaskan herring fillet processing
18) Non-Alaskan herring fillet processing
19) Abalone processing

3. Process Description

The processes used in this industry generally include the following: harvesting, storing, receiving, eviscerating, pre-cooking, picking or cleaning, preserving and packaging.

Harvesting utilizes some of the oldest and newest technologies in the industry. It may be considered a separate industry supplying the basic raw material for processing and subsequent distribution to the consumer. Harvest techniques vary according to species, and consist of four general methods: netting, trapping, dredging, and line fishing. Fishing vessels utilize the latest technology for locating fish and shellfish and harvest them in the most expedient and economical manner consistent with local regulations. Once aboard the vessel, the catch either is taken directly to the processor, or is iced or frozen for later delivery.

The receiving operation usually involves three steps: unloading the vessel, weighing, and transporting by conveyor or suitable container to the processing area. The catch may be processed immediately or transferred to cold storage.

Preprocessing refers to the initial steps taken before the raw material enters the plant. It may include beheading shrimp at sea, eviscerating fish or shellfish at sea, and other operations to prepare the fish for butchering.

Wastes from the butchering and evisceration are sometimes dry-captured, or screened from the waste stream, and processed as a fishery by-product.

Occasionally, cooking or precooking of crab or tuna may be practiced in order to prepare the fish or shellfish for picking and cleaning operation. The steam condensate, or stick water, from the tuna or crab precook is often collected and further processed as a by-product.

The fish is prepared in its final form by picking or cleaning to separate the edible portions from non-edible portions. Wastes generated during this procedure are sometimes collected and saved for by-product processing. Depending on the species, the cleaning operation may be manual, mechanical, or a combination of both. With fresh fish and fresh shellfish, the meat product is packed into a suitable container and held under refrigeration for shipment to a retail outlet. If the product is to be held for extended periods of time before consumption, several forms of preservation are used to prevent spoilage caused by bacterial action and autolysis: freezing, canning, pasteurization and refrigeration.

Bacterial growth is arrested at temperatures below $-9^{o}C$ ($16^{o}F$). For this reason, freezing is an excellent method of holding uncooked fish for an extended period of time. Freezing is also advantageous because the meat remains essentially unchanged, in contrast to canning, which alters the product form. However, autolysis still continues at a reduced rate, necessitating the consumption of the meat within approximately 6 months. Storage times vary from species to species. Cooking of crabs prior to freezing inactivates many enzymes and further slows autolysis.

Preservation by canning requires special equipment to fill the can, preservatives and seasonings, and a partial vacuum to seal the can. A partial vacuum is necessary to avoid distortion of the can due to increased internal pressures during cooking. After sealing, the cans are washed and retorted (pressure-cooked) at approximately 115°C (240°F) for 30 to 90 minutes, depending on the can size. Although the enzymes are inactivated at rather low temperatures, high temperatures must be reached to insure the destruction of harmful anaerobic bacterial spores. Clostridium botulinum, the most harmful of these, must be subjected to a temperature of 116°C (240°F) for at least 8.7 minutes. A longer cooking time is employed to achieve this temperature throughout the can and to insure total destruction of the bacteria. After the cook, the can is cooled with water and the canned fish or shellfish is transported to the labeling room for casing and shipment.

Industrial fishery products include such commodities as fish meal, concentrated protein solubles, oils, and also miscellaneous products including liquid fertilizer, fish feed pellets, kelp products, shell novelties and pearl essence. The major fish species used for producing industrial fishery products are the Atlantic menhaden and the Pacific anchovy.

Meal, oil, and solubles are extracted from the fish via a wet reduction process. This process consists of cooking the fish with live steam at about 240°F. The cooked fish are then pressed, separating the fish into press cake (solids) and press liquor (liquid). The press cake is dryed, ground and sold as fish meal. The press liquor is clarified and the oil is separated. The oil is then further refined, stored and shipped. The de-oiled press liquor, known as stickwater, is usually evaporated to about 50 percent solids and sold as fish solubles.

4. Wastewater Characterization

Table 8-4-1 contains raw wastewater characteristics for the industry. Pollutant parameters of concern are BOD, COD, TSS and oil and grease.

5. Control and Treatment Technology

In Plant Control - The major in plant control for this industry is the recovery of what is now wasted food stock. Much of the fish harvested is wasted even though it contains valuable protein which can be used for human or animal consumption.

TABLE 8-4-1
RAW WASTEWATER CHARACTERISTICS
CANNED AND PRESERVED SEAFOOD PROCESSING INDUSTRY

SUBCATEGORY	Flow GPD	BOD mg/l	COD mg/l	TSS mg/l	Oil & Grease mg/l
Farm-Raised Catfish	21M-45M	340	700	400	200*
Conventional Blue Crab	700	4400*	6300*	620	220*
Mechanized Blue Crab	20M-73M	600	1000	330	150*
Non-Remote Alaskan Crab Meat and Remote Alaskan Crab Meat	65M-99M	270	430	170	22
Non-Remote Alaskan Whole Crab & Crab Section and Remote Alaskan Whole Crab and Crab Section	36M-84M	330	710	210	30
Dungeness and Tanner Crab	38M-74M	280-1200*	550-2000*	60-130	28-600*
Non-Remote Alaskan Shrimp and Remote Alaskan Shrimp	300M-400M	1M*-2M*	2M*-3.7M*	1.3M-3M	100*-270*
West Coast Shrimp	90M-160M	2000*	3300*	900	700*
Southern Non-Breaded Shrimp	180M-240M	1000*	2300*	800	250*
Breaded Shrimp	150M-200M	720*	1200*	800	-
Tuna Processing	65M-3.6MM	700*	1600*	500	250*
Fish Meal	92M-10M[1]	100-24M[1]*	150-42M[1]*	70-20M[1]	20-5M[1]*
All Salmon	58M-500M	253-2600*	300-5500*	120-1400	20-550*
Bottom and Fin Fish (All)	6M-400M	200-1000*	400-2000*	100-800	40-300*
All Sardines	80M	1300*	2500*	921	250*
All Herring	29M	1200*-6000*	3000*-10,000*	600-5000	600*-800*
Hand Shucked Clam	86M-170M	800*-2500*	1000-4000*	600-6000	16-50
Mechanized Clam	300M-3MM	500-1200*	700-1500*	200-400	20-25
All Oysters	14M-320M	250-800*	500-2000*	200-2000	10-30
All Scallops	1M-115M	200-10,000*	300-11,000*	27-4000	15-25
Abalone	10M-14M	430-580	800-1000	200-300	22-30

NOTES:

1 - Higher range is for bailwater only
* - See Appendix C for parameters which may be inhibitory to biological systems
M = 1,000
MM= 1,000,000

Seafood processing wastewater may contain high concentrations of chlorides from processing water and brine solutions, and organic nitrogen (0-300 mg/l) from processing water.

There are also non-edible parts of fish such as the shells of shrimp and crab which contain chitin which can be recovered as a valuable product.

There are three major in-plant changes that would facilitate the recovery of now wasted valuable protein:

a) Minimizing the use of water (thus minimizing loss of solubles)
b) Recovery of dissolved proteins in effluent solutions
c) Recovery of solid portions for use as edible products.

The use of water may be minimized sometimes by substituting pneumatic transporting systems for water transporting systems. Another water saving technique is the use of spring loaded hose nozzles that automatically shut off when released by the operator. Presently hoses are frequently left running when not being used.

Protein can be recovered by use of one of the following techniques:

a) Conventional Reduction Processes
b) Protein Precipitation from Effluent Streams
c) Solids Recovery

Treatment Technology

The first major consideration in the design of treatment equipment is that solids removal should occur as quickly as possible. The longer the detention time between waste generation and solids removal the greater the BOD and COD and the smaller the by-product value.

Solids separation is generally accomplished by screening and sedimentation.

Other methods of treatment available to this industry consist of the following:

a) Activated Sludge
b) Trickling Filters
c) Aerated Lagoons
d) Land Disposal
e) Physical/Chemical Treatment such as
   Air Flotation

Table 8-4-2 provides a summary of removal efficiencies for some of these treatment techniques.

TABLE 8-4-2

CANNED AND PRESERVED SEAFOOD INDUSTRY
WASTE WATER TREATMENT PRACTICES

Pollutant and Method	Removal Efficiency, Percent
BOD	
Flotation	50-65
Biological Treatment	80-90
TSS	
Sedimentation	50-70
Flotation	30-87
COD	
Flotation	50-75

1. General Industry Description

The sugar processing industry includes the processing of raw cane sugar, the refining of liquid and crystalline cane sugar, and the processing of beet sugar. Cane sugar refineries produce either a white crystalline or a clear liquid sugar from unrefined raw sugar. Molasses is produced as a by-product. The raw materials for beet sugar processing are sugar beets, limestone, and small quantities of sulfur. The products are refined sugar, beet pulp and molasses.

The principal water usage in the cane sugar refining segment of the industry consists of barometric condenser cooling water, filter cake slurry, char wash, carbon slurries, boiler makeup, affination (wash) water, and ion exchange regeneration. In the beet sugar processing segment, water is used for six principal purposes: transporting or fluming beets to the processing operation, washing beets, processing (extracting sugar from beets), transporting lime mud cake waste, condensing vapors from evaporators and crystallization pans, and cooling. The sugar processing industry is covered by Standard Industrial Classification(SIC)2063.

2. Industrial Categorization

The sugar processing industry is broadly subdivided into two main categories: canesugar processing and refining, and beet sugar processing. Raw cane sugar processing is not covered in this discussion since these plants generally do not discharge into POTW's. Therefore, for the purposes of raw waste characterization and delineation of pretreatment information, the industry has been further subdivided into the following three subcategories:

Subcategory	Designation
Crystalline Cane Sugar Refining	(A)
Liquid Cane Sugar Refining	(B)
Beet Sugar Processing	(C)

3. Process Description

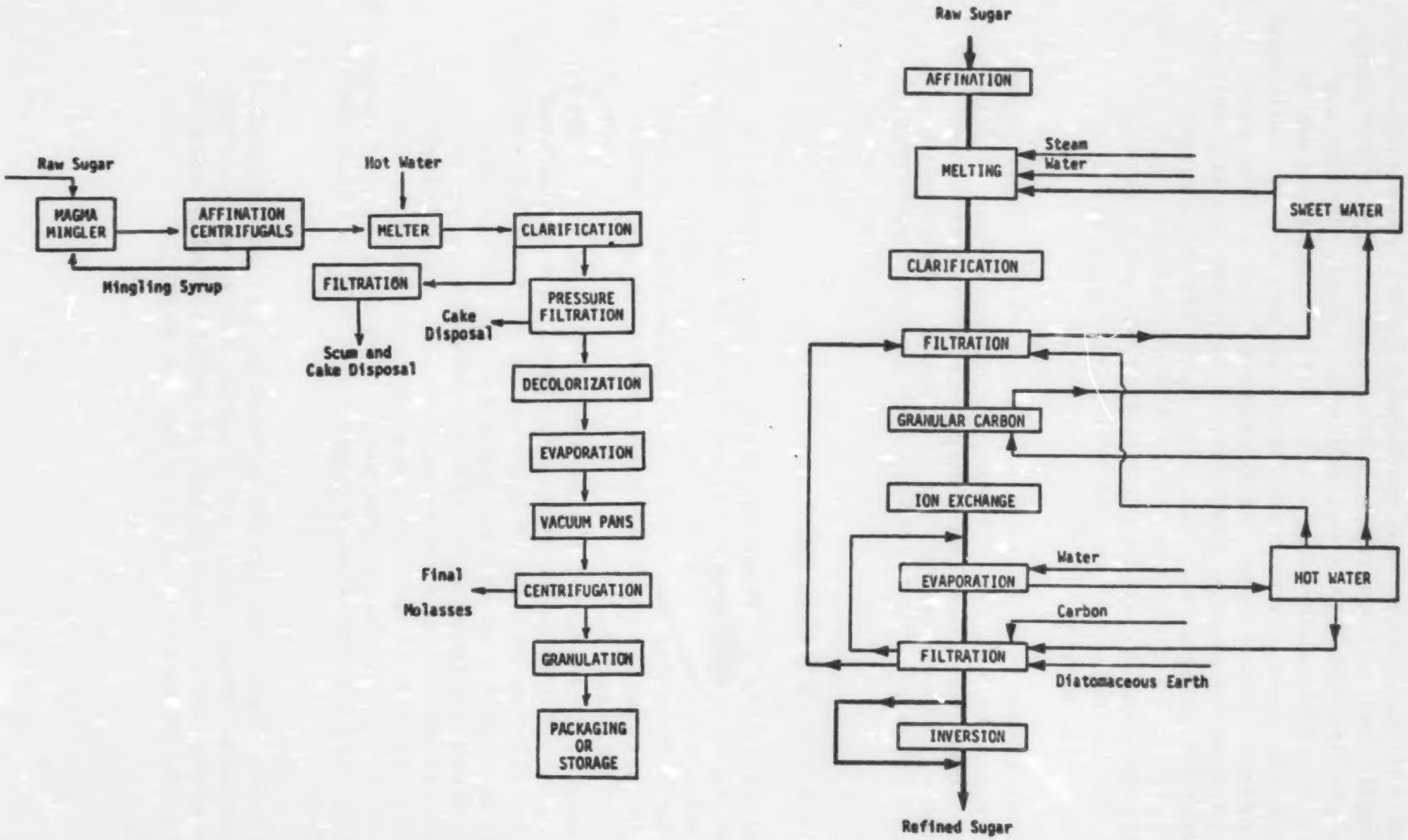
Crystalline Cane Sugar Refining (A)

The refinery receives raw crystalline sugar produced by the cane sugar factories. Raw sugar consists primarily of sugar crystals and various impurities which may include bagasse particles, organics, inorganic salts, and microorganisms. Sugar refining may be defined as the removal of the molasses film layer and associated impurities from the surface of the raw sugar crystals. The crystalline raw sugar is washed to remove part of the molasses film, then placed into solution, taken through various purification steps, and finally recrystallized. Figure 8-5-1 contains a process flow diagram for cane sugar refining.

Raw sugar crystals are placed in a magma mingler, (a mixer) in which magma (sugar syrup) is heated in order to facilitate loosening the molasses film from the raw sugar. The magma is fed into centrifugals which separate the syrup and molasses from the sugar. Hot water is added to wash the sugar which is then melted and screened. The remaining suspended and colloidal matter present in the melt liquor is removed by clarification. Clarification may involve coagulation and either flotation clarifiers or pressure filtration. The muds, scums, and filter muds produced in clarification contain significant sugar concentrations which must be recovered. The press cake is usually handled in a dry form and taken to landfill but may be slurried and sewered. After affination (washing) and clarification, the sugar liquor still contains impurities and color which are removed by adsorption.

Decolorization is accomplished by filtering sugar liquor through one of a variety of adsorptive materials including bone char, granulated activated carbon, powdered activated carbon, vegetable carbon, and ion exchange materials. After some period of operation, the decolorization ability of these materials decreases and they must be washed and regenerated. Sugar is recovered from the washwaters and the effluent is discharged. Granular carbon refineries use water for transporting the carbon. Transport water is reused but must be discharged periodically due to bacterial growth.

The final steps of recystallizing and granulating are essentially the same in all refineries. Recrystallization is performed by concentration of the decolorized sugar liquor and sweet water in continuous-type evaporators which are heated by steam, placed under vacuum, and operated in a series of several units. Short tube or calandria type evaporators are commonly used to achieve double or triple effect evaporation, although the Lillie film evaporator is also used in some installations.


Raw Sugar
MAGMA MINGLER
AFFINATION CENTRIFUGALS
Mingling Syrup
Hot Water
MELTER
CLARIFICATION
FILTRATION
Scum and Cake Disposal
PRESSURE FILTRATION
Cake Disposal
DECOLORIZATION
EVAPORATION
VACUUM PANS
CENTRIFUGATION
Final Molasses
GRANULATION
PACKAGING OR STORAGE
Raw Sugar
AFFINATION
Steam
Water
MELTING
SWEET WATER
CLARIFICATION
FILTRATION
GRANULAR CARBON
ION EXCHANGE
Water
EVAPORATION
HOT WATER
Carbon
FILTRATION
Diatomaceous Earth
INVERSION
Refined Sugar

CRYSTALLINE CANE SUGAR REFINING

LIQUID SUGAR REFINING

FIGURE 8-5-1
CANE SUGAR REFINING

Vapors from the last stage are condensed by one of several condenser designs, but all operate on the principle of relatively cold water passing through a cylindrical vessel, contacting the hot vapors, and condensing them. After concentration in evaporators, the sugar liquor and sweet waters are crystallized in single-effect, batch type evaporators called vacuum pans. Calandria pans are commonly used and are similar to the calandria evaporators except that the pans have larger diameters and shorter tubes in order to handle a more concentrated liquid. Finished crystalline sugar is produced by granulating and screening, and transported to conditioning silos prior to packaging or bulk shipment.

The principal wastewater streams in a crystalline cane sugar refinery are the barometric condenser cooling water, filter cake slurry, char wash, carbon slurry, truck and car wash, and floor wash. The condenser cooling water constitutes the largest volume of water used in a cane sugar refinery.

Liquid Cane Sugar Refining (B)

The initial refining steps of affination, decolorization, and evaporation in a liquid sugar refinery are essentially the same as described above for a crystalline sugar refinery. Since liquid sugar refineries do not recrystallize their primary product, the necessity of using vacuum pans is preempted, although some refineries use vacuum pans for the crystallization of remelt sugar, producing molasses as a by-product. After evaporation, the sugar solution is filtered and cooled and then sent to storage as liquid sugar. It may also be inverted to a specific degree and stored separately in stainless steel clad tanks equipped with ultra-violet lamps and air circulation filters to insure sterilization. The filtration and inversion processes are the same as those used in the formation of liquid sugar by the melting of crystalline sugar. A process flow diagram for liquid sugar refining is shown in Figure 8-5-1.

Because crystal formation is not a part of primary liquid sugar production, water usage to process the same quantity of raw cane sugar into liquid sugar is substantially smaller compared to the processing of crystalline sugar.

Beet Sugar Processing (C)

The raw materials for beet sugar processing are sugar beets, limestone, small quantities of sulfur, fuel and water. The products are refined sugar, dried beet pulp, and molasses. The basic steps for beet sugar processing consist of slicing, diffusion, juice purification, evaporation, crystallization, and recovery of sugar. A process flow diagram is shown in Figure 8-5-2.

Beets are delivered to the plant by trucks or railroad cars and stored in large piles or pumped directly into flumes for transport into the processing plant. The water flumes are provided with rock catchers which trap and remove stones and other heavy foreign material from the flume flow. The beets are next lifted from the flume to a washer by a beet wheel. The washed beets are sliced into thin ribbon-like strips called "cosettes", and fed into a continuous diffuser which extracts sugar and other soluble substances from the cossettes under a counter-current flow of water. The "raw juice" containing the sugar and other soluble substances is pumped to purification stations. The exhausted beet pulp is conveyed to pulp presses where its water content is reduced before being fed into pulp driers. Dried pulp is utilized as a base for livestock feed.

The raw juice from the diffusers is pumped to the first carbonation station. Lime, slaked lime, or calcium saccharate (from the Steffen process) is added and the juice is then saturated with carbon dioxide gas to precipitate calcium carbonate. The sludge thus formed is separated from the mixture by vacuum filters. The "thin juice", after further treatment with carbon dioxide, filtration, and sulfur dioxide to reduce the pH to about 8, is concentrated in multiple-effect evaporators to a "thick juice" and then boiled in a vacuum pan crystallizer to obtain the crystallized sugar. The sugar is separated by centrifugation from the adhering syrup and dried. The remaining syrup is further concentrated to yield additional sugar and molasses. The molasses may be added to the exhausted beet pulp or further desugarized by the Steffen process where the molasses is diluted, cooled and treated with calcium oxide to precipitate the sugar as a saccharate. The calcium saccharate, after separation by filtration from the remaining solution of impurities, is

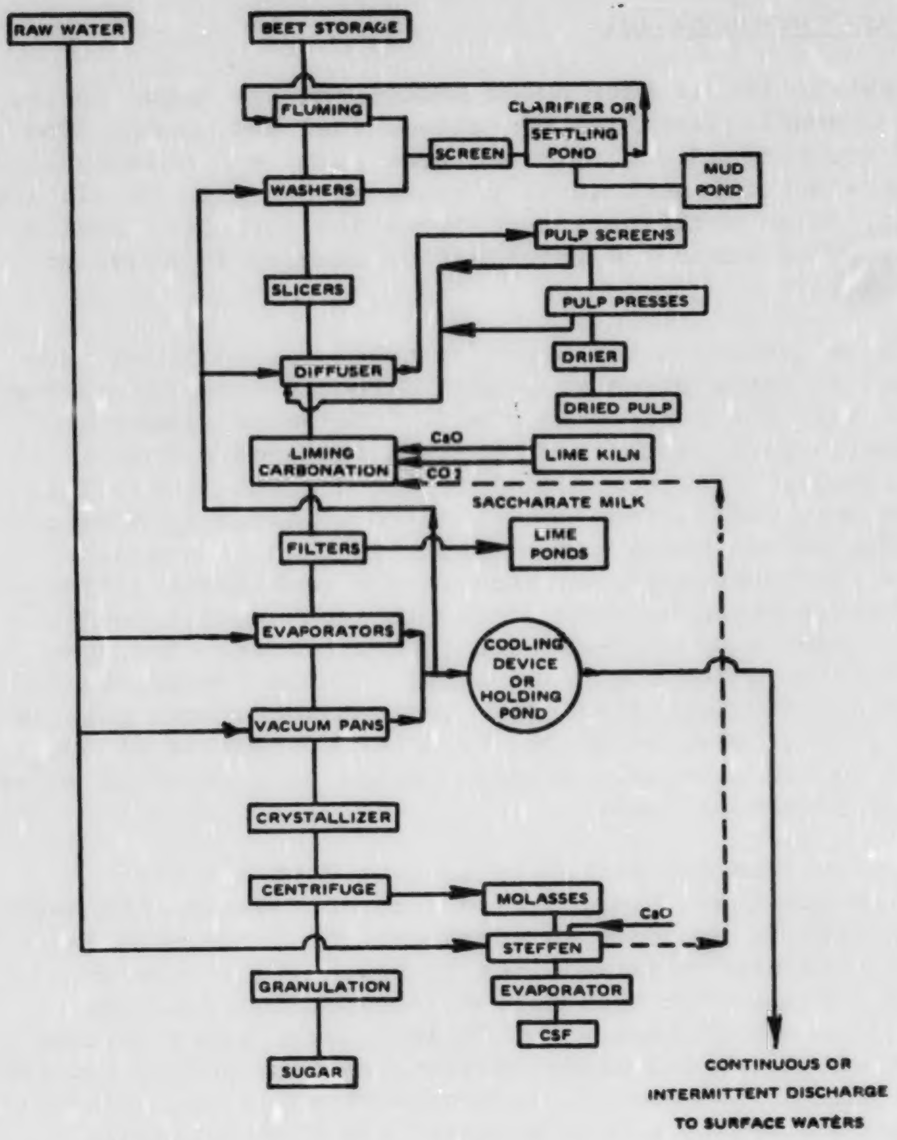

RAW WATER
BEET STORAGE
FLUMING
CLARIFIER OR SETTLING POND
SCREEN
MUD POND
WASHERS
PULP SCREENS
SLICERS
PULP PRESSES
DIFFUSER
DRIER
DRIED PULP
LIMING CARBONATION
CaO
CO 2
LIME KILN
SACCHARATE MILK
FILTERS
LIME PONDS
EVAPORATORS
COOLING DEVICE OR HOLDING POND
VACUUM PANS
CRYSTALLIZER
CENTRIFUGE
MOLASSES
CaO
STEFFEN
GRANULATION
EVAPORATOR
CSF
SUGAR
CONTINUOUS OR INTERMITTENT DISCHARGE TO SURFACE WATERS

FIGURE 8-5-2

FLOW DIAGRAM FOR A BEET SUGAR PROCESSING PLANT WITH SUBSTANTIAL IN-PROCESS RECYLE AND REUSE returned to the first carbonation station. Principal wastewater streams from a beet sugar processing plant consist of flume water, barometric condenser cooling water, pulp, mass and pulp screen water, lime cake slurry, and Steffen waste.

4. Wastewater Characterization

Wastewater characteristics of total effluents from each of the three subcategories of the sugar processing industry are shown in Tables 8-5-1 and 8-5-2.

5. Control and Treatment Technology

In-Plant Control - Significant in-plant control of both waste quantity and quality is possible for all three subcategories of the sugar processing industry. Important control measures in the cane sugar refining segment (A, B) of the industry include the prevention of sugar loss, improved techniques for dry-handling of sludges and filter cakes, maximum recovery and reuse of various process streams, and improved housekeeping practices. The unloading of raw sugar at the receiving area of a cane sugar refinery is often accompanied by sugar spillages, and the periodic washdown of the area produces a variable waste stream with a high content of sugar and BOD_5. Minimization of sugar spillage through equipment modification and the recovery of as much spilled sugar as possible by sweeping and improved housekeeping practices can essentially eliminate all sugar loss and the resulting pollutant load from the receiving area. A similar pollutant load resulting from truck and car wash can be minimized by maximizing the recovery of sucrose concentration from this waste stream for processing. Reduction of sucrose entrainment in the barometric condenser cooling water is a highly significant control measure. Barometric condenser water constitutes over 80 percent of the total water usage at cane sugar refineries (A, B), and sucrose entrainment represents an economic loss to the refiners as well as an organic pollutant load in the effluent. In calandria-type vacuum pans and evaporators, the vapor height should be at least 250 percent of the height of the calandria tubes to minimize entrainment. Where existing heights are insufficient, they can be increased by installing a spacer in the existing equipment. The liquid level in the vacuum pans and evaporators should be maintained near the design level. In addition to proper design and operation, a number of devices can be installed to separate liquid droplets from the vapors.

TABLE 8-5-1

SUGAR PROCESSING INDUSTRY
RAW WASTEWATER CHARACTERISTICS

Parameter	Crystalline Cane Sugar Refining (1) A	Liquid Cane Sugar Refining (1) B	Beet Sugar Processing C
Flow Range			
Flow Type	B	B	B
BOD_5 (mg/l)	13-263	72-487	857*
TSS (mg/l)	2-397	59-796	3,216
TDS (mg/l)	966 [2]	1,014* [2]	1,550*
COD (mg/l)	36-460	190-579	
NH_3 - N (mg/l)	0.46 [2]	0.03 [2]	
Kjel - N (mg/l)	0.60 - 1.66	0.51 [2]	
NO_3 - N (mg/l)	4.33 [2]		

Note:

* See Appendix 5 for parameters which may be inhibitory to biological systems

B-Batch Process

(1) These concentration ranges include both process wastewater and barometric condenser cooling water. Generally barometric condenser cooling water would not be discharged to a POTW, and consequently the pollutant values indicated would be correspondingly lower.

(2) Based on data from one plant only.

TABLE 8-5-2

SUGAR PROCESSING INDUSTRY
RAW WASTEWATER CHARACTERISTICS
BASED ON PRODUCTION

Parameter	Crystalline Cane Sugar Refining (1) A	Liquid Cane Sugar Refining (1) B	Beet Sugar Processing C
Flow Range (l/kkg)	3,300,-64,000	10,000-30,000	23,352
Flow Type	B	B	B
BOD_5 (kg/kkg)	0.63-2.4	2.2-5.1	20.0
TSS (kg/kkg)	0.06-12.5	0.94-8.4	55.8-94.1
TDS (kg/kkg)	46.9[2]	16.2[2]	70.0
COD (kg/kkg)	1.5-17.1	5.7-6.6	
NH_3 - N (kg/kkg)	0.02[2]	0 [2]	
Kjel - N(kg/kkg)	0.01-0.08	0.01[2]	
NO_3 - N (kg/kkg)	0.21[2]		

Note: l/kkg - liters of flow/1000 Kg product produced
kg/kkg - kilograms/1000 kg product produced
B - Batch Process

(1) These concentration ranges include both process wastewater and barometric condenser cooling water. Generally barometric condenser cooling water would not be discharged to a POTW, and consequently the pollutant values indicated would be correspondingly lower.

(2) Based on data from one plant only.

Baffle arrangements, which operate on either centrifugal or impingement principles, and demisters, which are essentially wire mesh screens serving the dual purpose of impingement and direction change, are examples of such devices. The use of partial surface condensers as heat exchangers in the exhaust ducts prior to barometric condensation is another entrainment control measure. These units not only affect liquid-vapor separation but also capture heat from the vapors. Most refineries use pressure filters such as the valley or industrial type for removing impurities from sugar liquors. In these refineries, a major portion of the filter cake can be recovered in a kiln by revivification of the filter aid.

In the beet sugar processing subcategory (C), important in-plant control measures include the proper handling of sugar beets, design of beet flume systems to facilitate dry-handling techniques, process water reuse, dry-handling of lime mud cake, conversion of Steffen filtrate to usable end-products, and the recovery and reuse of various flows in the plant. Removal of soil, leaves, and trash from the sugar beets in the field and delivery of the cleanest possible raw product to the plant is highly desirable. Without adequate control measures, late season irrigation and wet-field harvesting contribute to increased waste treatment needs and cost of settling devices in complete recycle flume water systems. Deterioration of sugar beets during storage should be minimized by maintaining proper conditions in the stockpiles and reducing storage time. Waste loads imposed upon the beet flume system can be reduced by minimizing the contact time between the sugar beets and the flume water or by the adoption of dry handling procedures. The typical flume water recycling system is a relatively inexpensive means of providing treatment for reuse and retention of flume water. The reuse of process wastewater (pulp press water, pulp transport water, wet pulp screen water) is an important control measure. Process waters can be reused for a variety of plant needs or returned to the diffuser. Pulp transport water can be eliminated by a dry conveyor system which moves exhausted pulp to the presses. Problems of fermentation and noxious odors associated with the long-term holding of lime mud wastes can be minimized by using shallow pond depths or aeration. Wastewaters associated with the barometric condensing operation can be reused as diffuser makeup water, raw water supply, beet flume recirculation makeup, lime mud slurrying water and gas wash water.

Treatment Technology

The various wastewater treatment practices for each of the three subcategories of the sugar processing industry are summarized in Table 8-5-3. The standard practice for urban cane sugar refineries, which represent about three-fourths of U.S. refined cane sugar production, is to discharge all waste streams other than barometric condenser cooling water to municipal treatment plants. However, it should be noted that direct discharges employ biological treatment of process water with or without blowdown from the barometric condenser cooling water recirculation system. Rural refineries generally have available land for impoundment, and total or partial wastewater retention is the standard practice. In beet sugar processing plants, treatment practices vary from little treatment to storage and land disposal of all wastes.

TABLE 8-5-3

SUGAR PROCESSING INDUSTRY WASTEWATER TREATMENT PRACTICES (Percent Removal)

Parameter & Practice	Crystalline Cane Sugar Refining A	Liquid Cane Sugar Refining B	Beet Sugar Processing C
BOD			
1. Total impoundage of all wastewaters	100	100	100
2. Impoundage of process wastewater	82	82	
3. Dewatering and dry hauling of filter slurry	26	26	
4. Screening, settling, and recycle of flume water, with mud drainoff to holding ponds for land disposal			96
5. Biological treatment of process wastewater	77	91	
6. Biological treatment of process wastewater and barometric condenser blowdown	95	96	
TSS			
1. Total impoundage of all wastewaters	100	100	100
2. Impoundage of process wastewater	100	100	
3. Dewatering and dry hauling of filter slurry	86	86	
4. Biological treatment of process wastewater	99	98	
5. Biological treatment of process wastewater and barometric condenser blowdown	99.6	99.7	
TDS			
1. Total impoundage of all wastewaters	100	100	100
COD			
1. Total impoundage of all wastewaters	100	100	100
Nitrogen			
1. Total impoundage of all wastewaters	100	100	100

1. Industry Description

The textile industry involves the manufacture of fabrics from wool, cotton, and synthetic fibers; the synthesis or spinning of synthetic fibers is not included in this group, but rather is included under synthetic organic chemicals.

The industry's basic raw materials are wool, cotton, and man-made fibers. Of the three major textiles, wool represents the smallest market and synthetic textiles the largest. The natural fibers are supplied in staple form (staple being short fibers). The man-made fibers are supplied as either staple or continuous filament. In either case, the fiber is spun into yarn which is simply a number of filaments twisted together. The yarn is woven or knitted into a fabric and the fabric then is dyed and treated to impart such characteristics as shrink resistance, crease resistance, fireproofing, etc. The finished fabric is delivered (directly or through converters, jobbers, and wholesalers) to the manufacturer of textile products.

This industry comprises the manufacturing activities listed under Standard Industry Classifications (SIC) 225, 226, 227, 228, 2211, 2221, 2231, 2241, 2295, 2296, 2297, 2298, 2299.

2. Industry Categorization

A useful categorization for the purposes of raw waste characterization and the establishment of pretreatment information are the following subcategories:

Process	Designation
Wool Scouring	A
Wool Finishing	B
Dry Processing	C
Woven Fabric Finishing	D
Knit Fabric Finishing	E
Carpet Mills	F
Stock and Yarn Dyeing and Finishing	G
Commission Finishing	H

3. Process Description

Figure 8-6-1 is a flow diagram for the textile industry showing the processes described below.

Wool Scouring (A)- Wool is a natural fiber of sheep origin and contains many impurities which must be removed before further use. Wool scouring, shown in Figure 8-6-2, is the process that converts the raw wool into cleaned wool yarns. After the fleece is sorted, it is carried through a series of scouring bowls where scour liquor flows countercurrent to it. Detergent is added to emulsify greases and oils. The scoured wool is dried and converted into wool top. The scour liquor contains significant quantities of oil and grease which does not appear to be readily biodegradable. It also contains materials derived from sheep urine, feces, blood, tars, branding fluids and insecticides, as well as grit. A grease recovery step is important to reduce pollution. Two methods are commonly used: centrifuging and acid cracking.

In centrifuging, the lowest density stream contains concentrated grease, which is recovered; the medium density stream is recycled as fresh scour liquor; the high density stream consists mainly of dirt and grit, and is sent to the treatment plant.

An alternative means to break the grease emulsion for wool grease recovery is the acid-cracking grease recovery system. The grease is recovered and the liquor is then neutralized and sent to the treatment plant.

Wastewaters contain significant quantities of oil and grease even after in-process recovery.

Wool Finishing (B) - The process flow diagram is shown in Fig. 8-6-3. This process converts wool fibers into finished wool fabric with washing, dying, weaving, knitting and the intermediate steps. Wool finishing has a higher water usage rate than any other fiber finishing category. Heavy scouring is the term applied to the washing of the fabric by the use of detergents, wetting agents, emulsifiers, alkali, ammonia, or other washing agents. The purpose of this heavy scour is to remove oils, grease dirt, etc. This process is one of the most important steps in wool finishing because if all of the foreign materials are not completely washed out, the finished fabric is susceptible to rotting, smelling, and bleeding, and will not accept dyes uniformly. Heavy weight, closely woven fabrics with a high percentage of recycled wool require very heavy detergents, long wash times and extensive rinsing to clean the goods. High organic and hydraulic loadings are associated with this type of fabric.

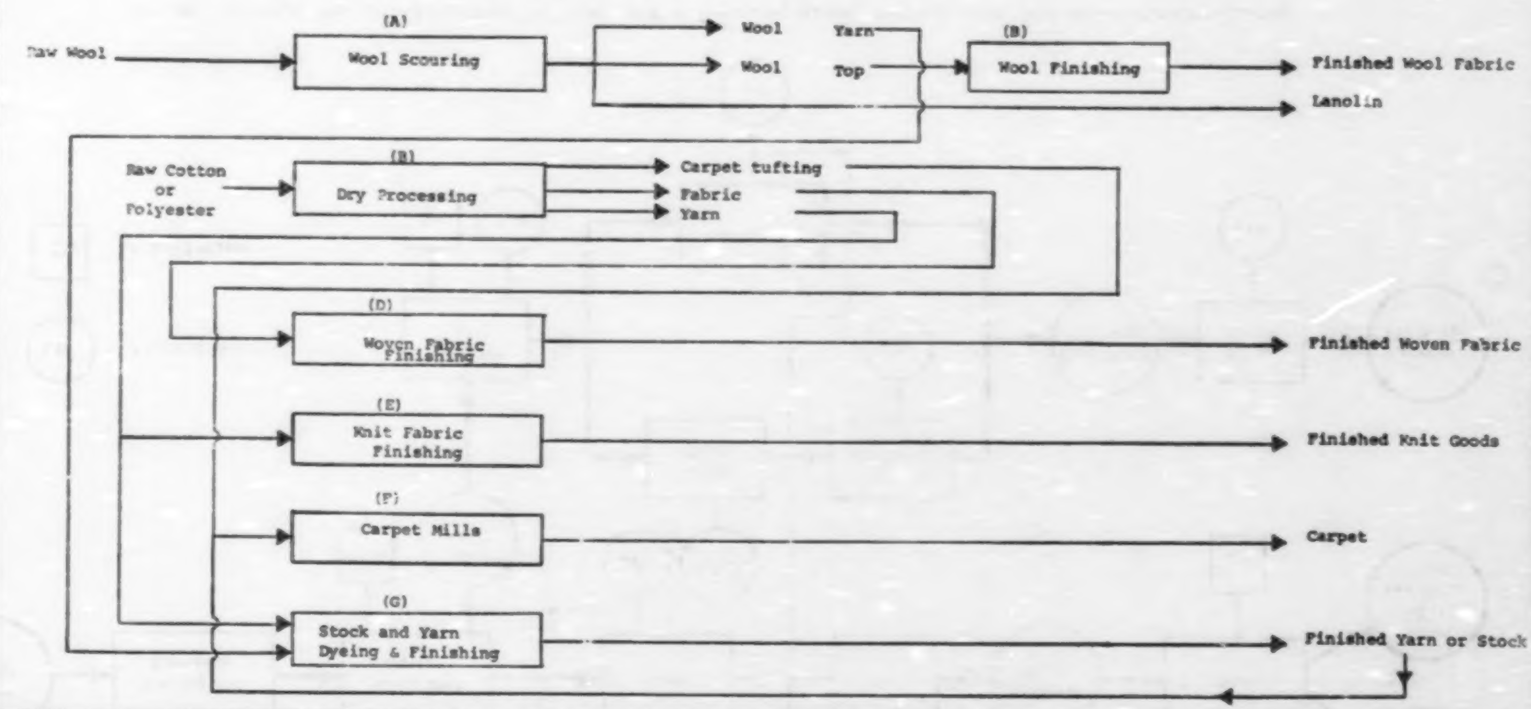
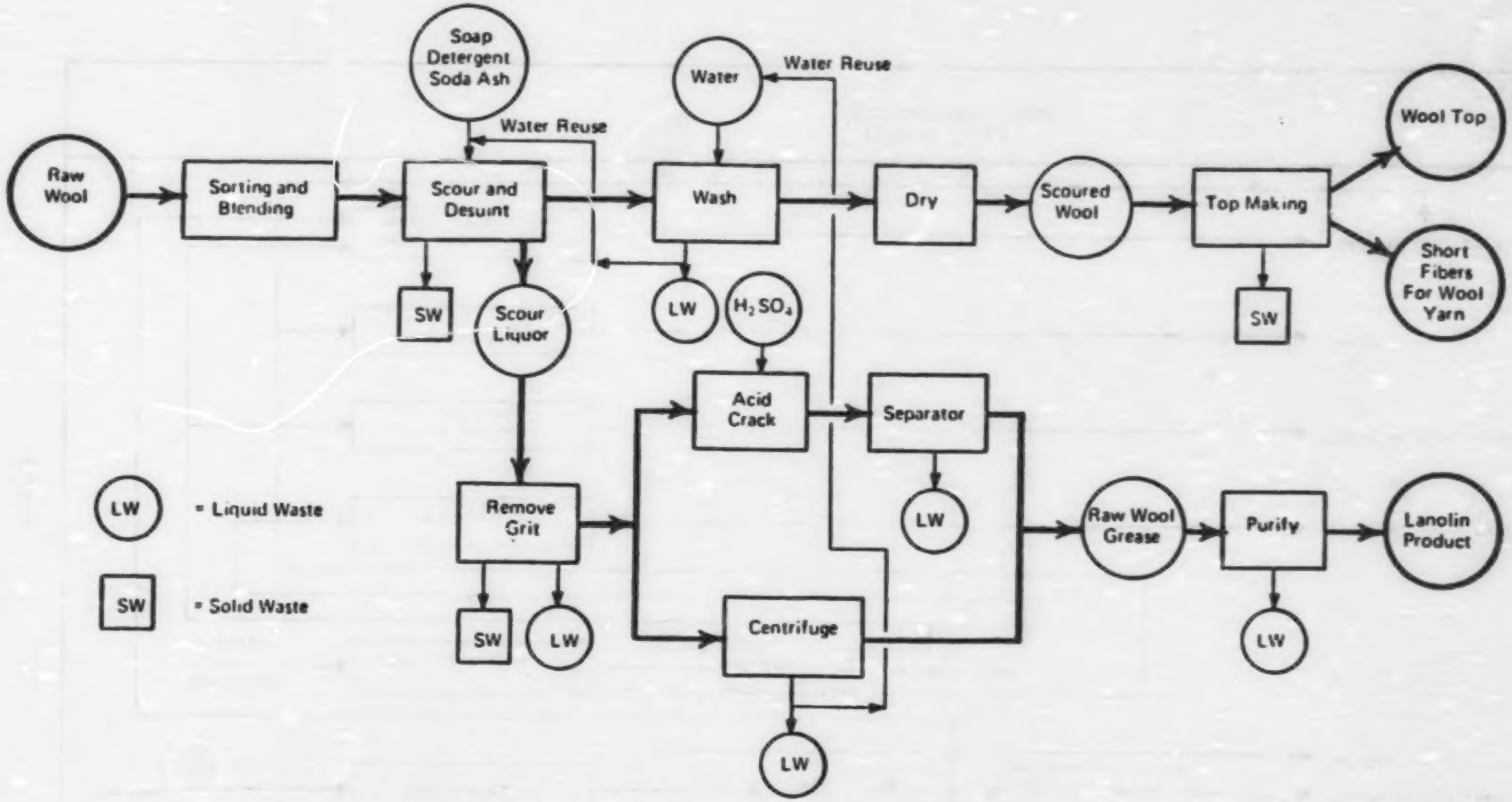

Raw Wool
(A)
Wool Scouring
Wool
Wool
Yarn
Top
(B)
Wool Finishing
Finished Wool Fabric
Lanolin
Raw Cotton or Polyester
(B)
Dry Processing
Carpet tufting
Fabric
Yarn
(D)
Woven Fabric Finishing
Finished Woven Fabric
(E)
Knit Fabric Finishing
Finished Knit Goods
(F)
Carpet Mills
Carpet
(G)
Stock and Yarn Dyeing & Finishing
Finished Yarn or Stock

FIGURE 8-6-1
TEXTILE MANUFACTURING



Raw Wool
Sorting and Blending
Soap Detergent Soda Ash
Water Reuse
Scour and Desuint
SW
Scour Liquor
Water
Water Reuse
Wash
LW
H_2SO_4
Dry
Scoured Wool
Top Making
SW
Wool Top
Short Fibers For Wool Yarn
Acid Crack
Separator
LW
Remove Grit
SW
LW
Centrifuge
LW
Raw Wool Grease
Purify
LW
Lanolin Product
LW = Liquid Waste
SW = Solid Waste

Source: "Chemical Physical and Biological Treatment of Wool Processing Wastes," by Hatch, et al, 28th Annual Purdue Industrial Waste Conference, West Lafayette, Indiana, 1 May 1973.

FIGURE 8-6-2
WOOL SCOURING (A)
TEXTILE INDUSTRY

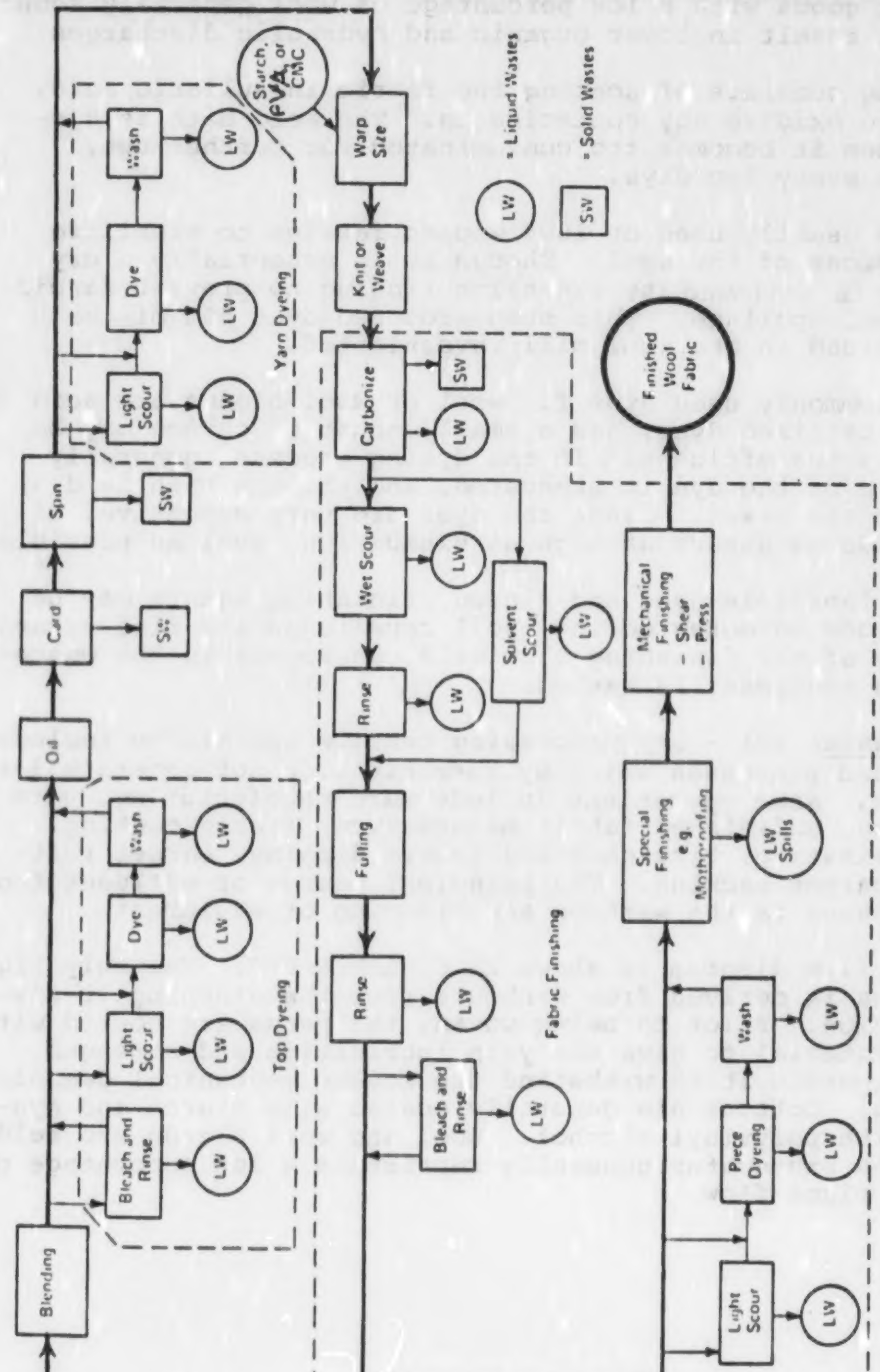

Wool Top
Blending
Bleach and Rinse
Light Scour
Dye
Wash
Top Dyeing
Oil
Card
SW
Spin
SW
Light Scour
Dye
Wash
Yarn Dyeing
Starch, PVA, or CMC
Warp Size
Knit or Weave
Carbonize
SW
Wet Scour
Rinse
Fulling
Rinse
Bleach and Rinse
Fabric Finishing
Solvent Scour
Mechanical Finishing Shear Press
Special Finishing e.g. Mothproofing
LW Spills
Light Scour
Piece Dyeing
Wash
Finished Wool Fabric
LW
LW = Liquid Wastes
SW = Solid Wastes

FIGURE 8-6-3
WOOL FINISHING (B)
TEXTILE INDUSTRY

Light open goods with a low percentage of wool generally scour easily and result in lower organic and hydraulic discharges.

Carbonizing consists of soaking the fabric in sulfuric acid, in order to oxidize any contaminants. The acid bath is discharged when it becomes too contaminated for further use, about once every two days.

Fulling is usually used on 100% woolen fabrics to stabilize the dimensions of the wool. Though it is essentially a dry process, it is followed by extensive rinsing to prevent rancidity and wool spoilage. This step produced over 50% of the hydraulic load in one wool mill investigated.

The more commonly used dyes for wool or wool blends are acid dyes or metallized dyes, and a small amount of chrome may be expected in the effluent. In the dyeing process, generally 90% or more of the dye is exhausted, and the dye bath is discharged to the sewer. Since the dyes are very expensive, effort is made to assure as high an exhaustion level as possible.

After the fabric is dyed and rinsed, finishing agents may be applied, such as mothproofing, soil repellents and fire retardents. Any of the finishing chemicals can appear in the wastewater when equipment is washed.

Dry Processing (C) - Dry processing textile operations include products and processes which by themselves do not generate large discharges. Some operations include yarn manufacturing, yarn texturizing, unfinished fabric manufacture, fabric coating, fabric laminating, tire cord and fabric dipping, carpet tufting, and carpet backing. The principal source of effluent from such processes is the washing and cleaning of equipment.

A process flow diagram is shown in Figure 8-6-4. The only liquid waste shown is derived from washouts from the slashing or sizing operation. Prior to being woven, the yarns are coated with a sizing material to give the yarn lubrication and strength that will permit it to withstand the severe mechanical demands of weaving. Cottons are generally coated with starch and synthetics with polyvinyl alcohol. Wool and wool blends are seldom sized. The wastewater generally represents a low percentage of the total plant flow.

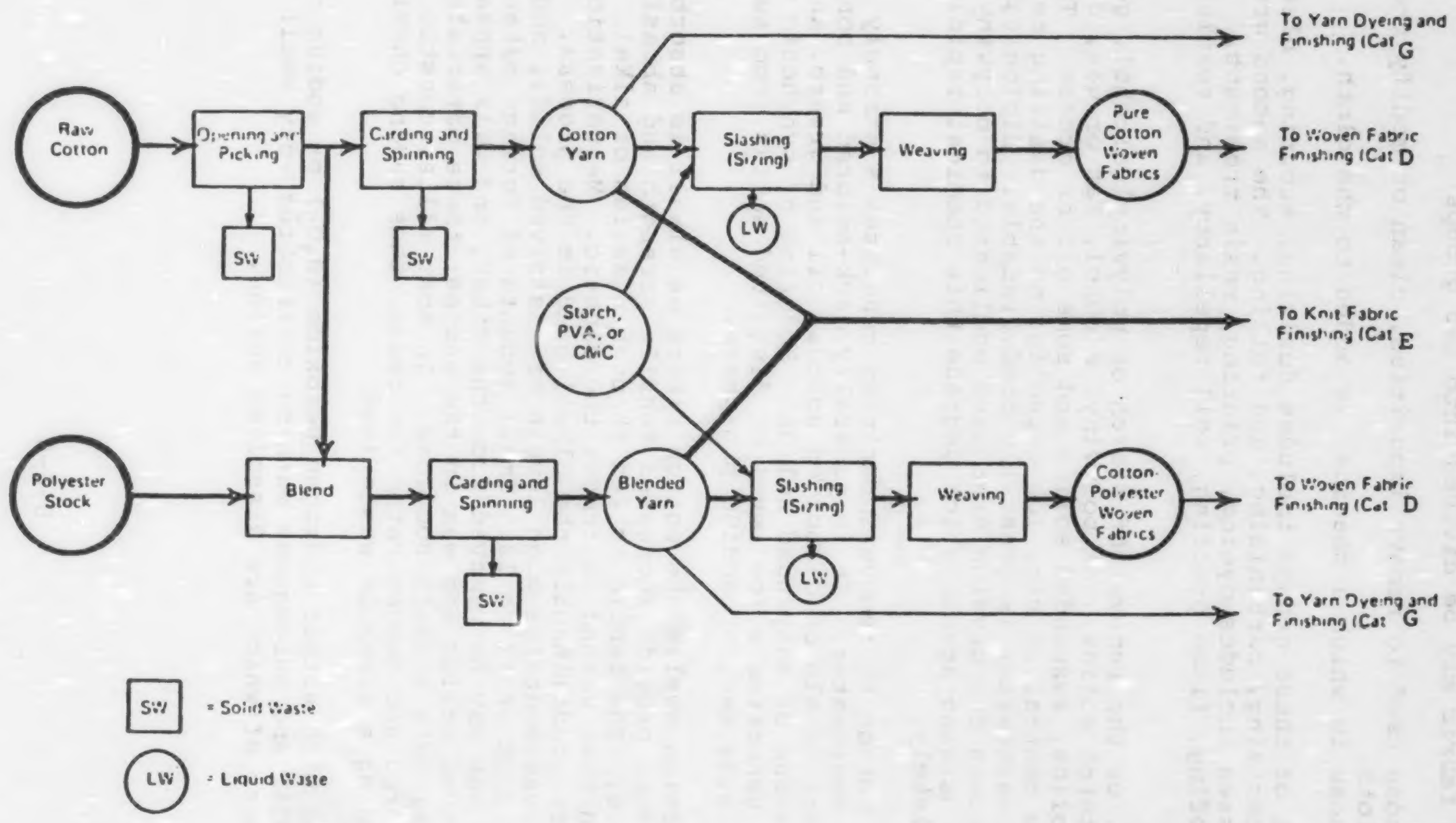

Raw Cotton
Opening and Picking
SW
Carding and Spinning
SW
Cotton Yarn
Slashing (Sizing)
LW
Weaving
Pure Cotton Woven Fabrics
To Yarn Dyeing and Finishing (Cat G
To Woven Fabric Finishing (Cat D
Starch, PVA, or CMC
To Knit Fabric Finishing (Cat E
Polyester Stock
Blend
Carding and Spinning
SW
Blended Yarn
Slashing (Sizing)
LW
Weaving
Cotton-Polyester Woven Fabrics
To Woven Fabric Finishing (Cat D
To Yarn Dyeing and Finishing (Cat G
SW = Solid Waste
LW = Liquid Waste

FIGURE 8-6-4
DRY PROCESSING (CLOTH GOODS) (C)
TEXTILE INDUSTRY

Woven Fabric Finishing (D) - A process flow diagram is shown in Figure 8-6-5. Wet Processes which are used in finishing woven fabric may be divided into two groups:

1. Those used to remove impurities, clean or modify the cloth.
2. Those in which a chemical is added to the cloth.

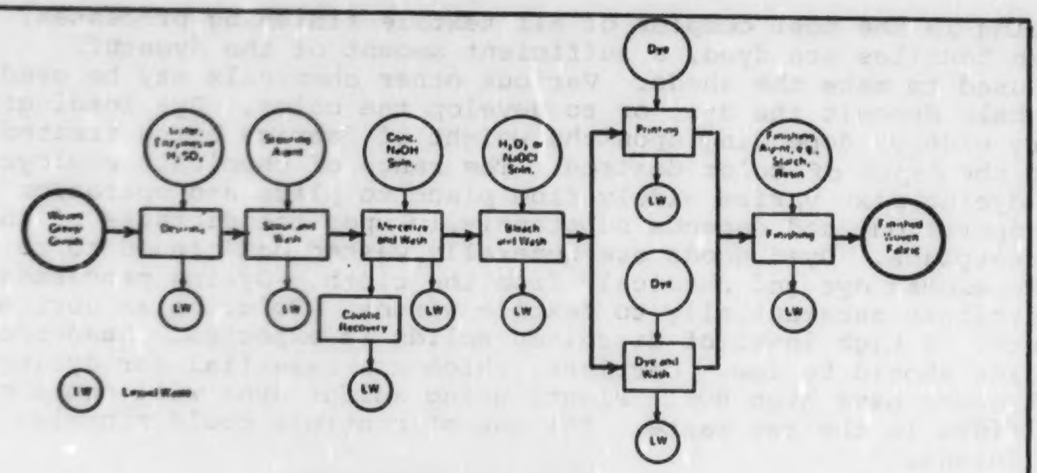
The first of these groups includes desizing, scouring, bleaching, mercerizing, carbonizing, and fulling. The second group of processes includes dyeing, printing, resin treatment, waterproofing, flame proofing, soil repellancy, and special finishes.

Desizing, or the removal of starch or polyvinyl alcohol, generates starch solids , or polyvinyl alcohol, fat or wax, dissolved solids, suspended solids and some oil or grease. The pH may be neutral or very low depending on the desizing method. The wastewater is generally biodegradable. Biological waste systems can develop organisms acclimated to polyvinyl alcohol (sizing agent) which degrade this chemical rapidly and completely.

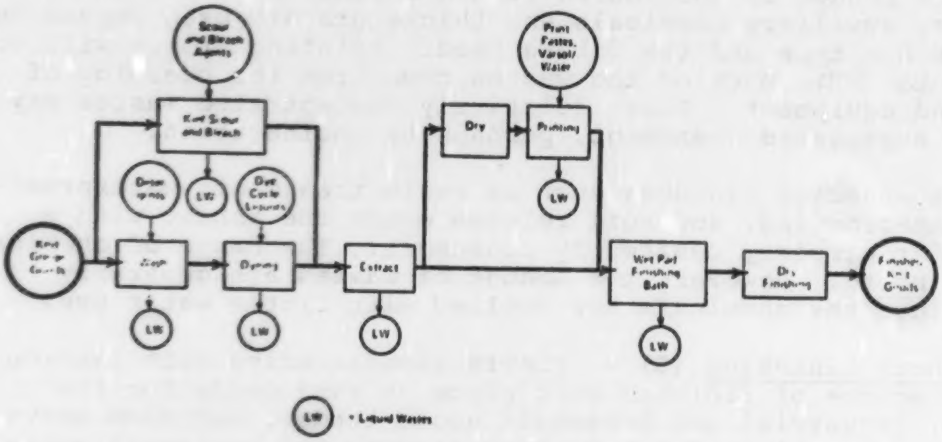
Scouring cotton to remove impurities generates a strongly alkaline wastewater. It is generally dark-colored and contains significant levels of dissolved solids, oil and grease, and a modest amount of suspended solids. Scouring of synthetic woven goods generates a low level of dissolved solids from surfactant, soda ash, or sodium phosphate.

Mercerization swells the cotton fibers as alkali is absorbed into them to provide increased tensile strength and abrasion resistance. The fabric is fed through a series of alkali baths and then washed to remove the caustic. Mercerization wastes are predominantly the alkali used in the process. The waste stream contains high levels of dissolved solids, and may have a pH of 12 to 13. Small amounts of foreign materials and wax may be removed from the fiber, and will appear as suspended solids and wax in the wastes; these materials will contribute a small BOD load. In most mills, caustic soda is recovered and concentrated for reuse, thus saving chemical and avoiding a sizeable waste load.

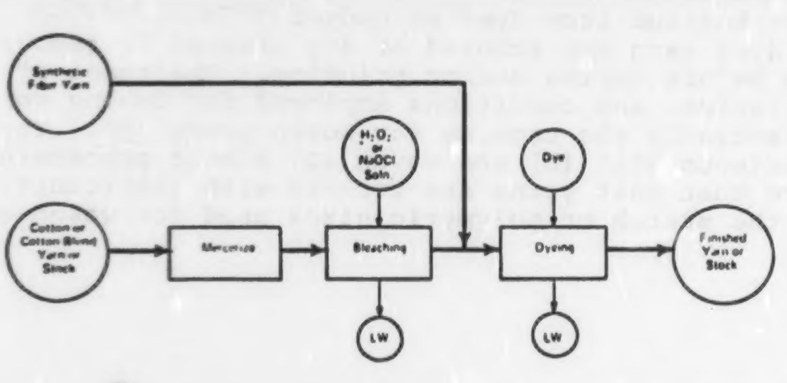
Bleaching with either hydrogen peroxide (H_2O_2) or sodium chlorite (NaOCl) and subsequent washing contributes very small waste loads, most of which are dissolved solids.


Woven Greige Goods
Water, Enzymes or H_2SO_4
Desizing
Scouring Agent
Scour and Wash
Conc. NaOH Soln.
Mercerize and Wash
Caustic Recovery
H_2O_2 or NaOCl Soln.
Bleach and Wash
Dye
Printing
Dye
Dye and Wash
Finishing Agent, e.g., Starch, Resin
Finishing
Finished Woven Fabric
LW
LW Liquid Waste

WOVEN FABRIC FINISH (D)


Knit Greige Goods
Scour and Bleach Agents
Knit Scour and Bleach
Detergents
Wash
Dye Cycle Liquors
Dyeing
Extract
Dry
Print Pastes, Varsol/Water
Printing
Wet Part Finishing Bath
Dry Finishing
Finished Knit Goods
LW
LW = Liquid Wastes

KNIT FABRIC FINISHING (E)


Synthetic Fiber Yarn
H_2O_2 or NaOCl Soln
Dye
Cotton or Cotton Blend Yarn or Stock
Mercerize
Bleaching
Dyeing
Finished Yarn or Stock
LW
LW = Liquid Wastes

Stock and Yarn Dyeing and Finishing (G)

FIGURE 8-6-5
TEXTILE FINISHING
TEXTILE INDUSTRY

Dyeing is the most complex of all textile finishing processes. When textiles are dyed, a sufficient amount of the dyestuff is used to make the shade. Various other chemicals may be used to help deposit the dye, or to develop the color. Dye loadings vary widely, depending upon the weight of fabrics being treated and the depth of color desired. The range of chemicals employed in dyeing also varies widely from place to place and operation to operation, and depends substantially upon the dictates of the marketplace. Dyed goods are generally washed and rinsed to remove excess dye and chemicals from the cloth. Dyeing processes contribute substantially to textile wastes. Color is an obvious waste. A high level of dissolved solids is expected. Suspended solids should be low. Carriers, which are essential for dyeing polyester have high BOD. Plants using sulfur dyes will contain sulfides in the raw waste. The use of controls could minimize pollutants.

Printing involves application of dyes or pigments in the form of a pattern on to fabric. Dyes penetrate and color the fiber; pigments are bonded to the fabric with a resin. In addition to the dyes, auxiliary chemicals and thickeners are used depending upon the dye type and the fibers used. Printing wastes will contribute to BOD. Much of the wastes come from the cleaning of tanks and equipment. These relatively concentrated wastes may justify segregated treatment, perhaps by incineration.

Finishing-Special finishes such as resin treatment, waterproofing, flameproofing, and soil release endow the fabric with a particular property desired by consumers. The range of chemicals is very broad. However, the amount of wastes are generally small since the chemicals are applied with little water use.

Knit Fabric Finishing (E) - Plants manufacturing knit fabrics are the source of finished knit piece or yard goods for the apparel, industrial and household goods trades, and also serve to augment supplies of fabric to underwear and outerwear manufacturers. A process flow diagram is shown in Figure 8-6-5.

Fabrics may be knitted from dyed or undyed yarns. Fabrics knitted from dyed yarn are scoured or dry cleaned to remove knitting oils before dyeing and/or printing. The types of dyestuffs, auxiliaries, and conditions employed for dyeing knit goods are essentially the same as for woven goods (D). The main differences between knit (E) and woven (D) fabric processing operations are that knit yarns are treated with lubricants rather than with the starch or polymeric sizes used for woven goods yarns, and that mercerizing operations are not employed with knit goods. Otherwise, the character of the wastes are similar to woven fabrics (D).

Carpet Mills (F) - The carpet industry wastes are very similar to those from Category E. When polyester is dyed, the carriers present a problem. Although steps are being taken to produce polyester fiber that can be dyed without carriers, disposal of carrier still remains a problem. The pH of carpet wastes is usually close to neutral. The hot dye wastes sometimes present a problem to biological treatment systems. The color problem is similar to that of other finishing categories. Where carpets are printed or dyed continuously, the thickeners present a high BOD load, as in fabric printing.

Carpet yarn is generally dyed in another mill and then brought to the carpet mill. The yarn is tufted onto a backing in a dry operation. Washing to remove residual dye, acid, thickeners, and other additives follows. Substantial amounts of dyes and chemicals may be in the effluent. The carpet is then ready for application of the backing. A process flow diagram is shown in Figure 8-6-6.

Stock and Yarn Dyeing and Finishing (G) - In this subcategory crude yarn is obtained from a spinning facility. The yarn may be natural, synthetic, or blended. Wet processes used by yarn mills include scouring, bleaching mercerizing, dyeing and finishing. Wastes generated will depend upon whether natural fibers, blends, or synthetics are processed. A process flow diagram is shown in Figure 8-6-5.

When synthetics are handled, only light scouring and bleaching is required, and wastes would contain low levels of BOD and dissolved solids. Dyeing would contribute a stronger waste, due to a carrier in the case of polyester and to some acetic acid. These wastes, of course, would also contain some color.

Scouring, bleaching, and mercerizing of cotton generate BOD and color because of the fiber impurities; and a level of dissolved solids because of the mercerizing.

Commission Finishing (H) - Commission finishing plants may process raw materials into products in any of the above textile subcategories. The common denominator is that these plants greige goods on a commission basis. The main difference between these plants and those of other subcategories is their ability to control the fabrics and finishing specifications demanded. Because "commission house" is an economic description of a plant, some "commission houses" can control the processing fabrics and are not characterized by extreme variability in

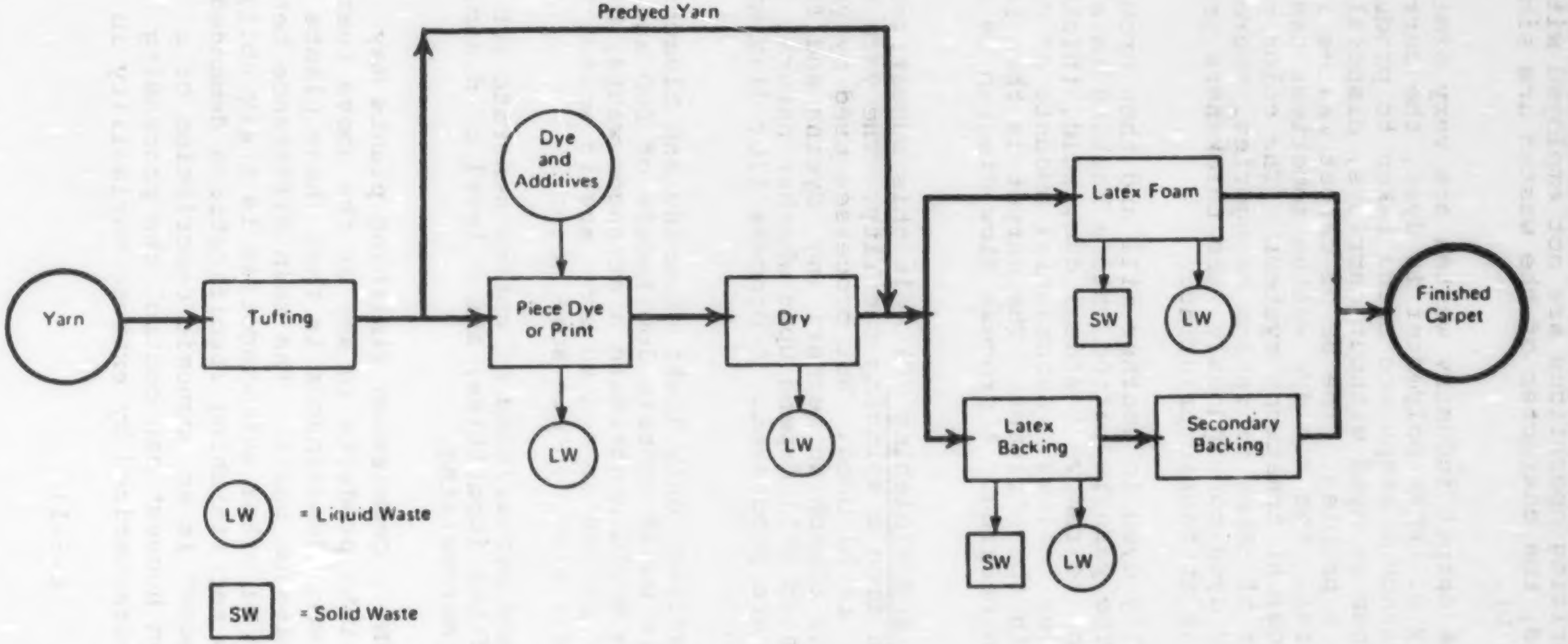

Yarn
Tufting
Predyed Yarn
Dye and Additives
Piece Dye or Print
LW
Dry
LW
Latex Foam
SW
LW
Latex Backing
SW
LW
Secondary Backing
Finished Carpet
LW = Liquid Waste
SW = Solid Waste

FIGURE 8-6-6
CARPET MILLS (F)
TEXTILE INDUSTRY

waste load and waste composition. Other "commission houses" cannot control the scheduling and flow of material through the plant, and these operations are characterized by an extremely high variability in waste load and composition. Thus, commission finishing subcategory plants are defined as manufacturers of textile materials owned outside their organization. Furthermore, commission finishing subcategory plants must produce 20 percent or more of their commission production from batch operations and process 50 percent of their commission orders in lots of 5,000 yards or less.

4. Wastewater Characterization

Textile wastes are generally colored, highly alkaline, high in BOD, suspended solids, coliform, and high in temperature. Some colors are water soluble and some are not. Biodegradibility is highly variable. Metals are used in some dyeing operations of the industry such as copper and chromium. Small amounts of zinc and magnesium salts may enter the waste stream from processes that produce durable press goods. Plants using sulfur dyes will discharge sulfides.

Wastewaters from commission finishing operations are generally similar to those produced by the finishing operations of the other subcategories. However, the treatability of these wastes is lower. This is due to the use of batch processing, rather than continuous processing, which requires more water; changes in raw materials being processed producing variable waste characteristics; extra rinses required between changes in raw material which increases the volume of discharge; and the finishing of special or "problem" materials, which require extra processing operations.

Tables 8-6-1 and 8-6-2 show textile wastewater characteristics.

5. Control and Treatment Technology

The control and treatment technology can be divided into two broad categories: in-process and end-of-pipe. Figure 8-6-7 is a waste treatment flow chart for cotton finishing wastes.

In-Plant Control - Practices to reduce the quantity and strength of textile wastes include good housekeeping, closer process control, process chemical substitution, and recovery.

Strict housekeeping procedures to minimize spills and wastes will reduce the load by only 5-10%, or more at some locations.

TABLE 8-6-1
TEXTILE INDUSTRY
RAW WASTEWATER CHARACTERISTICS[1]

Parameter(mg/l)	Wool Scouring A	Wool Finishing B	Dry Processing C	Woven Fabric Finishing D	Knit Fabric Finishing E	Carpet Mills F	Stock & Yarn Dying & Finishing G
BOD	1000-8000*	100-150	65-400	30-1800*	60- 750*	40-500	150- 600*
TSS	4000-10,000	25- 80	1-400	1- 800	30- 550	50-120	10- 50
COD	3000-30,000*		455-1000*	300-2500*	550-2000*	300-2500*	360-1400*
TDS	4000-15,000*		130-1600*	200-3700*	600-3500*	150-3000*	1000-2000*
Alkalinity	100-1900*		30-2000*	100-2100*	0- 500	90-300	100- 280
pH	12*			High	High	Neutral	
Oil	1000-6000*				50	12	
Sulfide	.1-1.0			.1-8			.6-2.4
Chrome			0-11*	3-28*	5*	.05-.67	.1-12*
Color		High		High	High	High	

Note:

[1] Data obtained from EPA files

*See Appendix 5 for parameters which may be inhibitory to biological systems.

TABLE 8-6-2
TEXTILE INDUSTRY

RAW WASTEWATER CHARACTERISTICS BASED ON PRODUCTION

Parameter	Wool Scouring A	Wool Finishing B	Dry Processing C	Woven Fabric Finishing D	Knit Fabric Finishing E	Carpet Mills F	Stock & Yarn Dying & Finishing G
Water Use gal/lb[1]	3.4	12.5	0.9	13.5	19.0	6	21.5
BOD kg/kkg[2]				20-140	16-50		15-48

Note:

[1] Gallons of water used/pound of production

[2] Kilograms of BOD/1000 kilograms of product manufactured

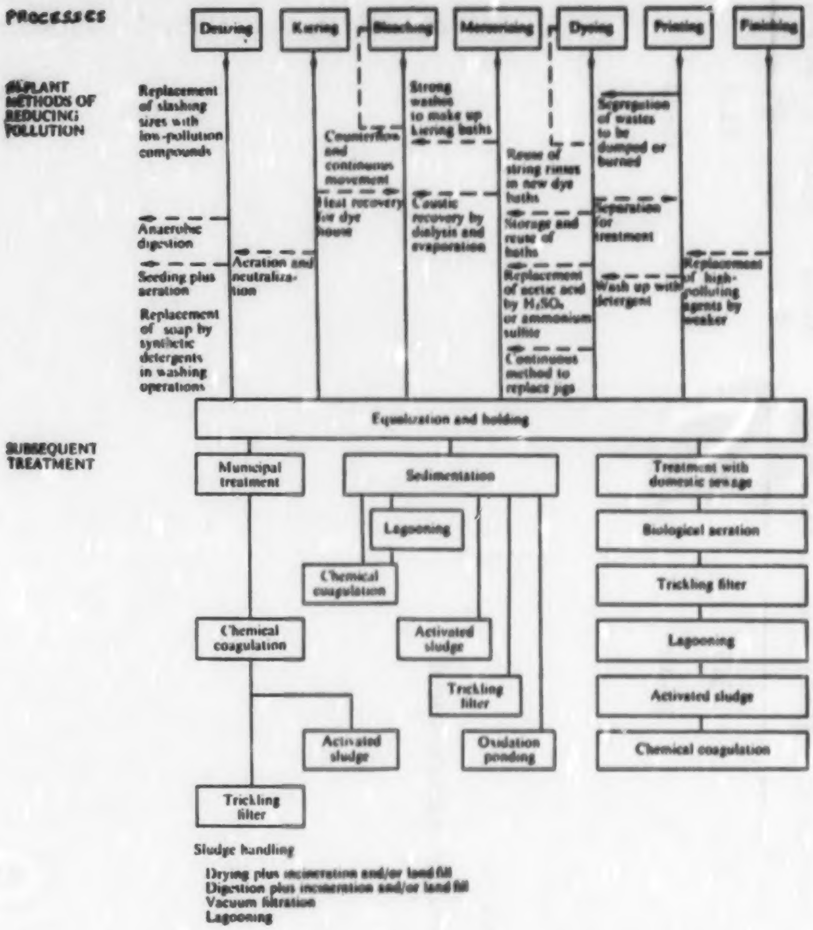

PROCESSES
Desizing
Kiering
Bleaching
Mercerizing
Dyeing
Printing
Finishing
INPLANT METHODS OF REDUCING POLLUTION
Replacement of slashing sizes with low-pollution compounds
Anaerobic digestion
Seeding plus aeration
Replacement of soap by synthetic detergents in washing operations
Aeration and neutralization
Counterflow and continuous movement
Heat recovery for dye house
Strong washes to make up kiering baths
Caustic recovery by dialysis and evaporation
Reuse of string rinses in new dye baths
Storage and reuse of baths
Replacement of acetic acid by H_2SO_4 or ammonium sulfite
Continuous method to replace jigs
Segregation of wastes to be dumped or burned
Separation for treatment
Wash up with detergent
Replacement of high-polluting agents by weaker
Equalization and holding
SUBSEQUENT TREATMENT
Municipal treatment
Chemical coagulation
Activated sludge
Trickling filter
Sedimentation
Lagooning
Chemical coagulation
Activated sludge
Trickling filter
Oxidation ponding
Treatment with domestic sewage
Biological aeration
Trickling filter
Lagooning
Activated sludge
Chemical coagulation
Sludge handling
Drying plus incineration and/or land fill
Digestion plus incineration and/or land fill
Vacuum filtration
Lagooning

FIGURE 8-6-7
COTTON TEXTILE FINISHING WASTE TREATMENT CHART

Closer control in the amount of chemicals used, as well as reduction in water usage may reduce pollution loads up to 30%. About 80% of all the water usage in textile wet processing is used for scouring. Water usage can be improved by utilizing the so-called "double-laced" box washers or in some cases by introducing counter-current washing flow schemes.

Chemical substitution is an important consideration in reduction of pollution. In some cases, it may be possible to substitute water with solvents such as perchloroethylene and trichloroethylene for conventional aqueous scouring practices.

Solvent scouring and finishing of knit fabrics is being practiced increasingly. The use of solvents minimizes liquid effluent wastes but it also requires strict air pollution control methods.

Recovery is an important consideration in any waste treatment plant. Caustic soda, steam and soaps can be recycled. Saleable glucose may be recovered from starch, and lanolin from wool grease. Suint can be recovered and sold to detergent manufacturers. Recovered fat might be rendered or used as a fuel source.

Polyvinyl alcohol (PVA) size wastes are being economically recovered in some plants so size wastes are expected to soon disappear.

The use of pressure dyeing vats in place of atmospheric units permits reduction in the amount of dye carriers required, thereby reducing the BOD and heavy metal concentration.

Treatment Technology - Generally both physical-chemical and biological methods are the treatment methods used by the textile industry. Alum, ferrous sulfate, ferric sulfate, or ferric chloride are used as coagulants, in conjunction with lime or sulfuric acid for pH control. Calcium chloride has also been found effective in coagulating wool scouring (A) wastes. Biological treatment methods which are used in the textile industry include activated sludge, trickling filter, anaerobic processes, aerated lagoons and rotating biological contractors.

One synthetic dying/finishing mill reports an 80% BOD removal efficiency and a 38% COD removal efficiency with an aerated lagoon treatment system. The two completemy mixed deep lagoons produce an effluent of constant and predictable quality, which is discharged to the municipal treatment syste. The long detention time of about 17 days allows equalization and treatment in the same unit process. Equalization storage of 24 hours allows the municipal plant operator the flexibility of choice in industrial effluent receipt. Capital construction costs and operating expense are reported to be less than other processes of comparable capacity.

In another study in a cotton finishing plant, washing and rinsing wastes were segregated from concentrated dyeing and finishing baths, and the more dilute wastewater for in-plant reuse. By treatment of this wastewater in aerated lagoons, and by neutralization, flocculation, filtration and adsorption, a colorless turbidity-free effluent is obtained meeting quality requirements for in-plant reuse. To avoid excessive salinity build-ups, part of the effluent has to be withdrawn from the recycle system, but 70% of the effluent can be recycled. The estimated cost of treatment is comparable to that of fresh water supply. Table 8-6-3 contains removal efficiencies achieved by various wastewater treatment practices for this industry.

TABLE 8-6-3

TEXTILE INDUSTRY WASTEWATER TREATMENT PRACTICES

	Removal Efficiencies (%)	
Pollutant and Method	Wool Scouring & Finishing A + B	Finishing D, E, G
BOD		
1. Chemical Coagulation	20 - 80	25 - 60
2. Activated Sludge	85 - 90	70 - 95
3. Trickling Filtration	80 - 85	40 - 85
4. Lagoons	0 - 85	50 - 95
5. Sedimentation	30 - 50	5 - 15
6. Oxidation Pond		30 - 80
Grease		
1. Grease Recovery:		
Acid Cracking	40 - 50	
Centrifuge	24 - 45	
Evaporization	95	
2. Sedimentation	80 - 90	
3. Flotation	95 - 98	
4. Lime + $CaCl_2$ Coagulation	97	
Suspended Solids		
1. Grease Recovery	0 - 50	
2. Sedimentation	50 - 65	15 - 60
3. Flotation	50 - 65	
4. Chemical Coagulation	80 - 95	30 - 90
5. Activated Sludge	90 - 95	85 - 95
6. Trickling Filter	90 - 95	80 - 90
7. Lagoons	30 - 70	50 - 95
Color		
1. Filtration + Carbon Adsorption		98 - 100

1. Industry Description

The cement industry produces various types of Portland cement for the construction industry. The raw materials for the production of cement include lime, silica, alumina, and iron. These materials, in chosen proportions, are ground, blended and heated in a kiln. Establishments engaged in cement manufacturing are included in Standard Industrial Classification (SIC) 3241.

2. Industrial Categorization

Although cement manufacturing does not generate a process wastewater stream, it does generate kiln dust, cooling water and wastewater from clean up operations. It is the dust handling process that is the source of significant wastewater loadings. Consequently this industry is subcategorized along dust handling lines.

Subcategory	Designation
Nonleaching	(A)
Leaching	(B)
Material Storage Runoff	(C)

3. Process Description

Cement is manufactured by a continuous process, normally interrupted only to reline the kilns. There are three major steps in the production process:

1. Grinding and blending of raw materials
2. Clinker production
3. Finish grinding

There are two (2) types of processes in the manufacture of cement -- "wet" and "dry". In the wet process the raw materials are ground together with water, fed to the kiln in a slurry and the water is evaporated. In the dry process, the raw materials are dried before grinding and are ground dry and fed to the kiln in a dry state.

The clinker is the fused product from the kiln which is then ground to make cement. No process wastewaters are generated. A process flow diagram is in Figure 8-7-1.

All cement plants collect large amounts of dust from the kiln. The high velocity gases flowing through the kiln carry large quantities of this dust which are then removed by collectors including cyclones, electrostatic precipitators,

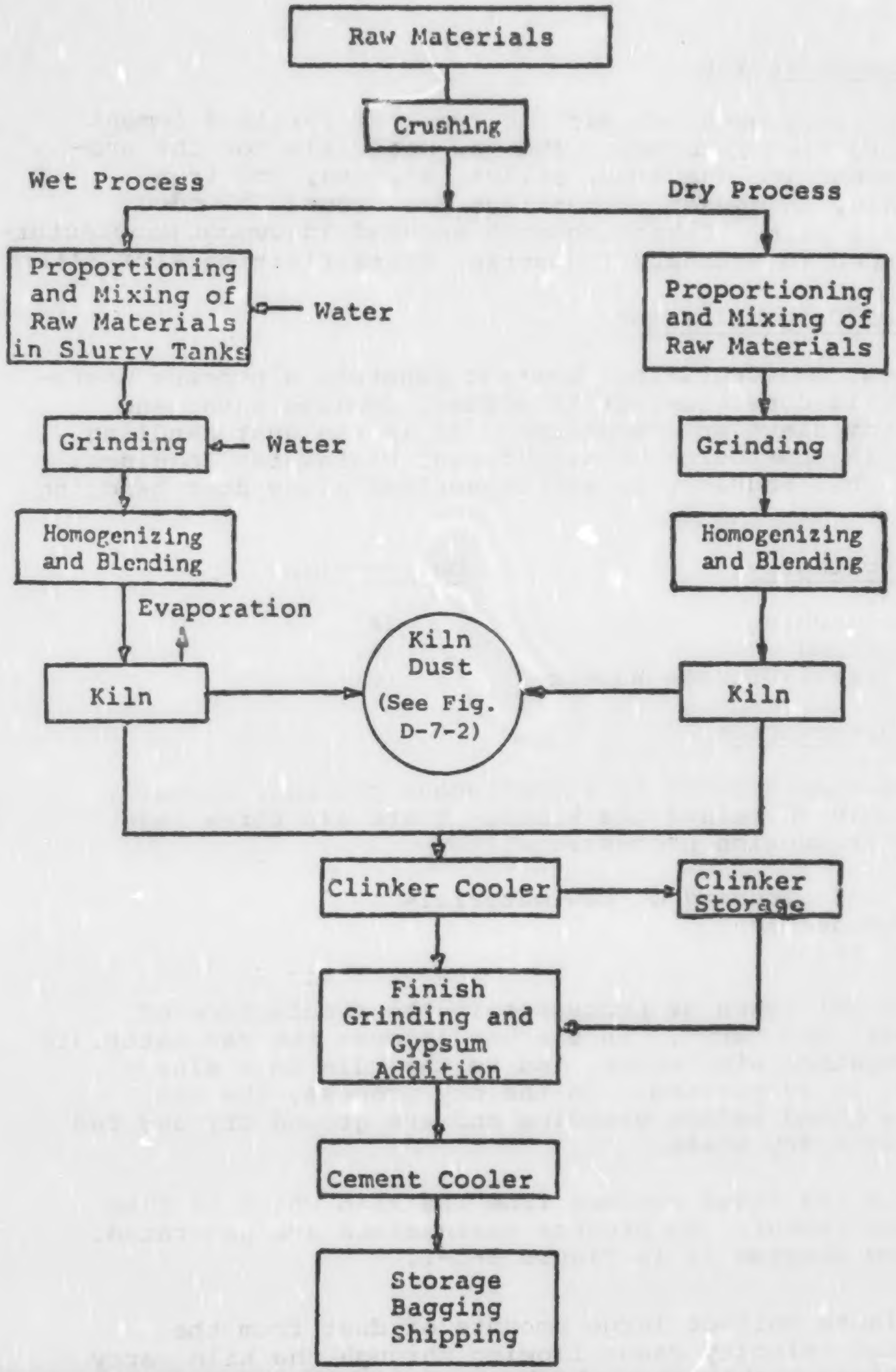

Raw Materials
Crushing
Wet Process
Dry Process
Proportioning and Mixing of Raw Materials in Slurry Tanks
Water
Proportioning and Mixing of Raw Materials
Grinding
Water
Grinding
Homogenizing and Blending
Homogenizing and Blending
Evaporation
Kiln
Kiln Dust (See Fig. D-7-2)
Kiln
Clinker Cooler
Clinker Storage
Finish Grinding and Gypsum Addition
Cement Cooler
Storage Bagging Shipping

Figure 8-7-1 Flow Sheet for the Manufacture of Portland Cement

bag filters and wet scrubbers. This dust is either recycled to the kiln or wasted. Some dusts contain an excessive alkali content and must be leached before reuse(B). If the kiln dust is not reused, it is disposed of by dry piling(A). Figure 8-7-2 is a flow diagram for Kiln Dust Collection and Handling for both leaching and nonleaching unit operations.

Nonleaching Plants (A) - Those manufacturing plants which dispose of kiln dusts in a manner in which there is no water contamination are included in this subcategory. Dry piling does produce runoff, however, which is discussed under the Materials Storage Subcategory (C).

Leaching Plants (B) - Those operations in which the kiln dust comes into direct contact with water are included in this subcategory. The three leaching operations which generate high wastewater loads include:

1. Leaching to remove soluble alkalies.
2. Wet disposal of dust.
3. Wet scrubbers for air pollution control.

(1) Leaching - The most significant of these operations is the leaching (removal) of soluble alkalies from the collected dust so that the dust may be returned to the kiln as recovered raw material. In all cases the overflow (leachate) from this operation is discharged, sometimes without treatment. The constituents include high pH, alkalinity, suspended solids, dissolved solids, potassium, and sulfate.

(2) Wet Disposal - The second most common operation is the wet disposal of dust. In this operation a slurry is also made of the collected kiln dust and fed to a pond, where the solids settle out. The settled solids are not recovered for return to the kiln, and the overflow (leachate) may be discharged. The constituents of this discharge are essentially the same as those from the leaching operation.

(3) Wet Scrubbers - The use of wet scrubbers for air pollution control constitutes the third example of water in direct contact with the kiln dust. Wet scrubbers collect kiln dust from effluent gases. Discharges contain the same contaminants as those from leaching.

Materials Storage Runoff (C) - Runoff from kiln dust piles, coal and raw materials piles may become contaminated if not properly contained or treated. Some runoff may result from routine clean-ups of accumulated dust or spraying of roads.

4. Wastewater Characterization - Tables 8-7-1 and 8-7-2 contain wastewater characteristics based on concentrations and production for the cement industry.

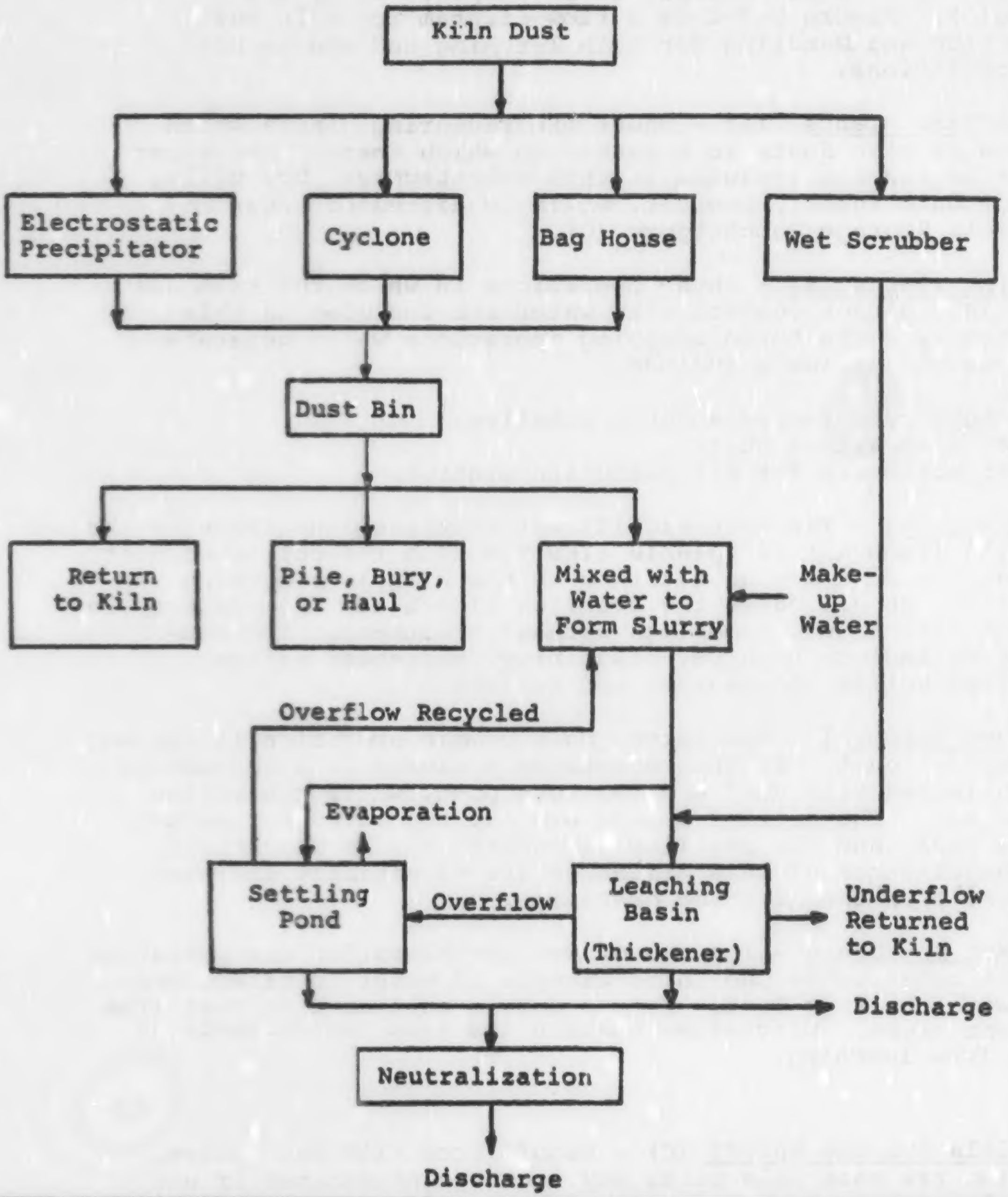

Kiln Dust
Electrostatic Precipitator
Cyclone
Bag House
Wet Scrubber
Dust Bin
Return to Kiln
Pile, Bury, or Haul
Mixed with Water to Form Slurry
Make-up Water
Overflow Recycled
Evaporation
Settling Pond
Overflow
Leaching Basin (Thickener)
Underflow Returned to Kiln
Discharge
Neutralization
Discharge

Figure 8-7-2 Kiln Dust Collection and Handling

TABLE 8-7-1
CEMENT MANUFACTURING
RAW WASTEWATER CHARACTERISTICS

Parameters	Nonleaching A	Leaching B
Flow (gpd)	500M-7MM	5MM-75MM
Flow Type	C	C
BOD (mg/l)	0	0
TSS (mg/l)	0	30
COD (mg/l)	0	1
pH	High	High
Alkalinity (mg/l)	30	45
Total Solids (mg/l)	100	225
Chromium (mg/l)	0	3
Lead (mg/l)	0	35 *
Aluminum (mg/l)	3	20
Iron (mg/l)	50 *	150 *
Potassium (mg/l)	25	100

NOTE:

C	Continuous
M	Thousand
MM	Million

*Usually present only if oyster shells are utilized in the manufacturing process.

TABLE 8-7-2

CEMENT MANUFACTURING
WASTEWATER CHARACTERISTICS BASED UPON PRODUCTION

Parameters [1]	Nonleaching A	Leaching B
Flow (l/kkg)	2M-3M	2.2M-30M
Flow Type	C	C
BOD (kg/kkg)	0	0
TSS (kg/kkg)	0	.9
COD (kg/kkg)	0	.03
Alkalinity (kg/kkg)	.09	1.4
Total Solids (kg/kkg)	.3	7.5
Chromium (kg/kkg)	0	.08
Lead (kg/kkg)	0	1
Aluminum (kg/kkg)	.01	.64
Iron (kg/kkg)	.16	4.8
Potassium (kg/kkg)	.08	3.3

NOTE:

1	kg/kkg kilogram pollutant/1000 kg product manufactured
M	Thousand
MM	Million
C	Continuous

5. Control and Treatment Technology

In-Plant Control Measures - With the exception of leaching operations cement plants can achieve virtually complete reuse of wastewater. Control technology for leaching operations consists of segregation of leaching streams and conservation of water to minimize the volume of water requiring treatment.

Temperature reduction of cooling waters has been accomplished in cooling towers, spray ponds, and storage ponds.

Precautions to enclose the dust disposal area with dikes to contain runoff will prevent runoff from kiln dust piles. Spraying the dust pile with latex and coal pile with tar can minimize water contamination.

Treatment Technology - Current technology can adequately control pH, alkalinity and suspended solids, but not dissolved solids from leaching plants.

Neutralization of the leachate water by the addition of mineral acids such as sulfuric acid has the following effects: it lowers pH to any desired level; it eliminates alkalinity; it dissolves some particulate matter such as lime. However, it adds to the total dissolved solids.

Carbonation of the leachate with stack gas lowers the pH, reduces the hardness, and the dissolved solids.

Several processes that might be employed to reduce dissolved solids in leaching plants include evaporation, precipitation, ion exchange, reverse osmosis,electrodialysis, and combinations of these. Some of these processes have technical limitations;i.e. ion exchange generates large amounts of waste material and the dissolved solids content of the leachate is too high for reverse osmosis to be practical.

Evaporation of the leachate could potentially eliminate the effluent. Although solar evaporation has low operating costs, it is applicable only in arid climates where a large amount of land is available. Evaporation by submerged combustion or heat exchangers involves considerable cost. Waste heat from the kiln might be employed for evaporation.

Electrodialysis, a technology to concentrate leachate appears promising. It produces a concentrated brine that can be evaporated and a stream suitable for recycling to the leaching system.

The retention of runoff from materials storage piles may be achieved by dikes or ditches with direct runoff into a retention pond where solids can settle. The effluent may be neutralized and treated before discharge.

1. General Industry Description

Animal production has evolved to the point where animals are raised on large, highly efficient industrial "feedlots", where animals, kept in high densities, are fed rations that will provide the fastest weight gains.

A feedlot is defines as follows:

A. A high concentration of animals held in a small area for periods of time in conjunction with one of the following purposes:

a. Production of meat

b. Production of milk

c. Production of eggs

d. Production of breeding stock

e. Stabling of horses

B. Transportation of feeds to the animals for consumption.

C. By virtue of the confinement of animals or poultry, the land or area will neither sustain vegetation nor be available for crop or forage production.

Animal species produced in feedlots include cattle (beef and dairy), swine, chickens, turkeys, ducks, sheep and horses.

This industry includes Standard Industrial Classifications (SIC) 0211, 0213, 0214, 0251, 0252, 0253, 0259, and 0272.

2. Industrial Categorization

The feedlot industry is divided into the following subcategories:

Subcategory	Designation
All subcategories except ducks	A
Ducks	B

3. Process Description

Cattle, swine, chickens, turkeys, ducks, sheep and horses are produced on open or housed feedlots.

Open Lot

An open lot is one in which the animals are either exposed to the outside environment or in which a relatively small portion of the feedlot offers some protection. The limited protection afforded may be in the form of a windbreak, shed type building with a roof and one to three sides enclosed, roof only, or some type of latticework shade.

The floor of an open feedlot may be dirt with a flat or slightly inclined surface. Figure 8-8-1 contains a sketch of an open lot.

Housed Lot

A housed feedlot is a building in which animals are kept under a roof at all times. Buildings may have sides which are either entirely open or completely enclosed. The floors can be of solid dirt or concrete construction, or may have slotted floors. Solid floor facilities utilize bedding material to absorb the excreted wastes. Slatted floors use a shallow pit beneath the floor for daily waste removal, or they may use deep pits for waste storage. Figure 8-8-1 contains a sketch of a housed lot.

Dairy cattle are milked twice daily and require milking facilities including transfer, storage and cooling equipment. Wastes can be collected and field spread. Wastewater discharges may be generated from milking center washups, and runoff from precipitation on exposed contaminated surfaces.

Ducks are raised in wet and dry lots. A wet lot is one in which the ducks have full access to swimming water for improvement in the quality of feathers.

4. Wastewater Characterization

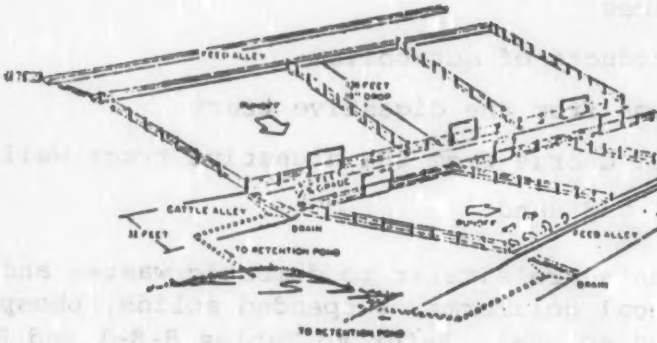
Feedlot wastes are generated from:

a. Bedding or litter (if used) and animal hair or feathers

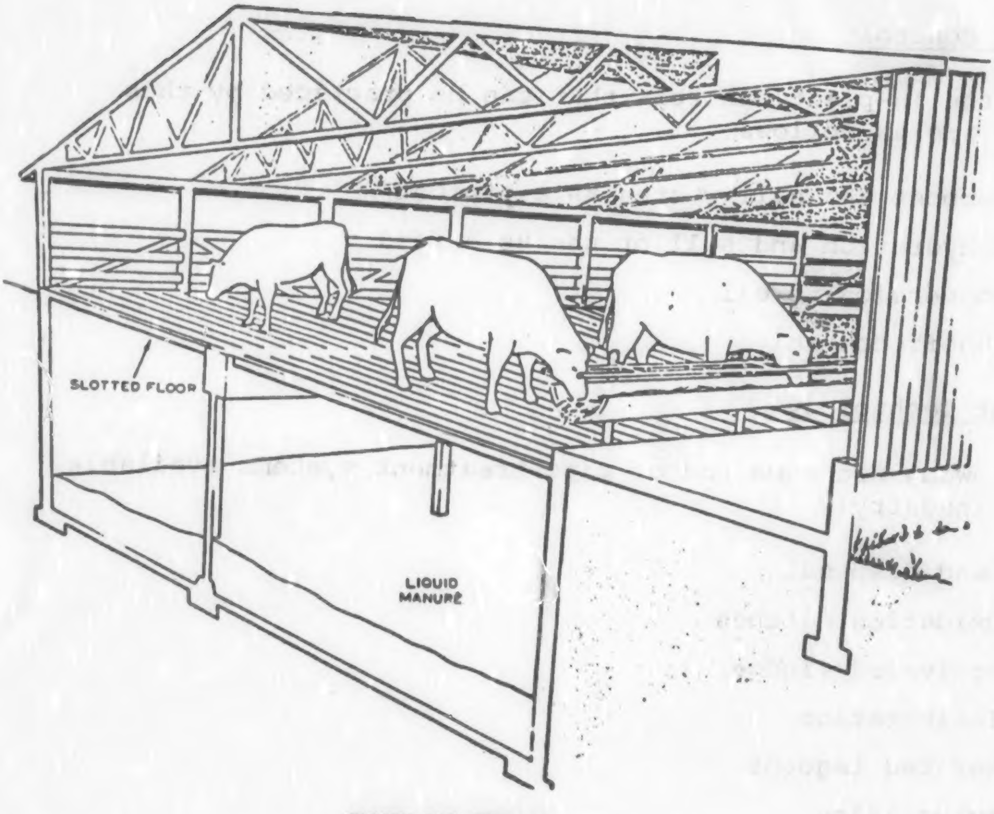
b. Water and milking center wastes

c. Spilled feed

d. Undigested or partially digested food or feed additives


FEED ALLEY
RUNOFF
CATTLE ALLEY
DRAIN
TO RETENTION POND
RUNOFF
FEED ALLEY
DRAIN
TO RETENTION POND

SKETCH OF A CHARACTERISTIC OPEN BEEF FEEDLOT FACILITY


SLOTTED FLOOR
LIQUID
MANURE

CLOSED LOT FEEDLOT

Figure 8-8-1

FEEDLOTS

e. Digestive juices

f. Biological products of metabolism

g. Micro-organisms from the digestive tract

h. Cells and cell debris from the digestive tract wall

i. Residual soil and sand

Wastewater constituents are similar to domestic wastes and contain BOD, COD, fecal coliforms, suspended solids, phosphorus, ammonia and dissolved solids. Refer to Tables 8-8-1 and 8-8-2 for wastewater characterization of feedlots.

5. Control and Treatment Technology

In-Plant Control

Some of the in-plant controls that can be practiced by this industry are as follows:

a. Compost and sell wastes as a product

b. Dehydration and sell or use as a feed

c. Conversion to oil

d. Runoff control

Treatment Technology

The following are some end of pipe treatment systems available to this industry:

a. Land disposal

b. Oxidation ditches

c. Activated sludge

d. Incineration

e. Aerated Lagoons

f. Evaporation

g. Trickling Filters

The high concentration of solids present in animal waste can vary all the way from semi-solid wastes containing 50% moisture scraped from floors to the liquid wastes resulting from runoff

TABLE 8-8-1
RAW WASTEWATER CHARACTERISTICS
FEEDLOT INDUSTRY

WASTE PARAMETER (mg/l)	Beef Cattle Open Lot Runoff	Dairy Cattle Milk Wastes	Swine Manure	Swine Runoff	Sheep and Lambs Manure	Sheep and Lambs Runoff	Ducks Wet Lot
Flow Type	B	B	C	B	C	B	C & B
BOD	1,700*	4,000*	2.5M*-20,000*	100	7,000*	3M* - 12M*	500
TSS	35,000	2,400	9,000	260	35M	8,000	4,000
COD	4,000*	No Data	6M* - 40M*	300	100M*	10M* - 80M*	7,500*
pH	7.6	8	8.5	7-8	7	7 - 8	7 - 8
Total Nitrogen	200	450	3,000	20	800	1,000	50
Ammonia Nitrogen	70	130	900-3M*	10	300	100 - 2M*	No Data
Total Phosphorous	90	60	400	5	400	80 - 750	70
Total Potassium	400		600	10	2,000*	700 - 2,000*	No Data
Magnesium	110		Trace	2	300	20	No Data
Ash	4,000		5M-12M	2	15M	6M - 18M	No Data

Note: *See Appendix 5 for parameters which may be inhibitory to biological systems.
Some Subcategories have been grouped together.
No data are available for Turkey Runoff.
The remaining Subcategories produce only Dry Waste.

M - Thousand
MM - Million

B - Batch
C - Continuous

TABLE 8-8-2

WASTE CHARACTERIZATION-FEEDLOT INDUSTRY
Units Based on Production

WASTE PARAMETER	SUBCATEGORY					
	Beef Cattle Manure	Beef Cattle Runoff	Dairy Cattle Manure	Dairy Cattle Milk Wastes	Swine Manure	Swine Runoff
	lbs/head/day	lb/head/inch runoff	lbs/head/day	lbs/head/day	lbs/head/day	lbs/head/inch runoff
Flow	48	1,200	50-630	30	5-110	900
BOD	1	2	1-2	1.2	0.14	0.5
TSS	-	7.6	>.16	0.08	0.2	1.2
COD	3.5	4	>6	No Data	0.2	1.3
pH	7.3	7.6	5	8	8.5	7-8
Total Nitrogen	0.27	0.2	0.2 - 0.4	0.04	0.02	0.1
Ammonia Nitrogen	0.08	0.07	0.2 - 0.3	0.005	0.02	0.04
Total Phosphorous	0.07	0.1	>0.04	0.002	0.012	0.02
Total Potassium	0.2	0.02	>0.2	No Data	0.02	0.02
Magnesium	0.02	0.1	>0.04	No Data	Trace	Trace
Ash	2	4	>1	No Data	0.1	0.3

Note: Some Subcategories have been grouped together.

TABLE 8-8-2 (Continued)

WASTE CHARACTERIZATION-FEEDLOT INDUSTRY
Units Based on Production

WASTE PARAMETER	SUBCATEGORY							
	Chickens, Broilers Layers, Breeders-Manure	Sheep and Lambs Manure	Sheep and Lambs Runoff	Turkeys Manure	Turkeys Runoff	Ducks Manure	Ducks Wet Lot	Horse Manure
	lbs/lb/day	lbs/head/day	lbs/head/inch runoff	lbs/head/day			lbs/head/day	lbs/head/day
Flow	0.06	30	160	1.5	No Data	No Flow	1,000	80
BOD	0.005	0.2	0.5	0.9			0.06	0.8
TSS	No Data	1	0.7	No Data			0.2	No Data
COD	0.02	3	2	0.3			0.3	4
pH	No Data	7	7-8	6.7			7-8	7
Total Nitrogen	0.01	0.03	0.2	0.02			0.006	0.6
Ammonia Nitrogen	No Data	0.01	0.02	0.01			No Data	0.2
Total Phosphorous	0.01	0.01	0.02	0.02			0.02	0.1
Total Potassium	0.01	0.3	1	0.006			No Data	0.6
Magnesium	0.0003	0.01	0.02	0.006			No Data	0.8
Ash	No Data	0.5	1	0.9			No Data	10

Note: Some Subcategories have been grouped together.

containing 2% solids. Animal waste, because of its high solids concentration, if added in significant quantities to a municipal system which operates with waste flows containing about 0.1% solids, will exceed the design capability of the primary treatment systems unless special provisions are made.

Because large solids concentrations may be present, secondary treatment systems such as trickling filters could become clogged and not capable of functioning while activated sludge systems would probably operate with impaired performance. A judgement should be made on an individual basis as to the amount of animal waste which should be allowed to enter a particular treatment system. Consideration should be given to the specific solids type and concentration in the animal waste, the present municipal waste load, and the treatment system and component capacity available to insure that a proper degree of dilution is maintained and the system's operational capacity is not exceeded.

1. General Industry Description

The metal finishing industry utilizes chemical and electrochemical operations to effect an improvement in the surface and structural properties of metals and other materials. These operations include: coatings on surfaces by electrodeposition; electroless plating; anodizing; chemical conversion techniques such as phosphating, chromating and immersion plating; and special contours or finishes obtained by electrochemical processes such as chemical milling and etching.

Wastewater from metal finishing processes comes from rinses following cleaning, pickling, plating and etching operations, and the waste streams contain concentrations of the basis material being finished as well as the components in the processing solutions. Occasional dumps of contaminated baths are also a waste source. Contaminants include metal cations (copper, nickel, chromium, zinc, lead, tin, cadmium, gold, silver, platinum metals, etc.) and their associated anions, such as phosphates, chlorides and cyanide.

Establishments engaged in this industry are covered by Standard Industrial Classification (SIC) 3471.

2. Industrial Categorization

This industry has been divided into two major categories, and a total of six subcategories as follows:

Major Category	Subcategory	Designation
Electroplating	Common Metals (copper, nickel, chromium, zinc, tin, lead, aluminum, etc.)	A
	Precious Metals (silver, gold, platinum, rhodium, iridium, and ruthenium)	B
	Specialty Metals (beryllium, magnesium, calcium, tellurium, rhenium, cobalt, and mercury)	C
Metal Finishing	Anodizing	D
	Coatings	E
	Chemical Etching and Milling	F

3. Process Description

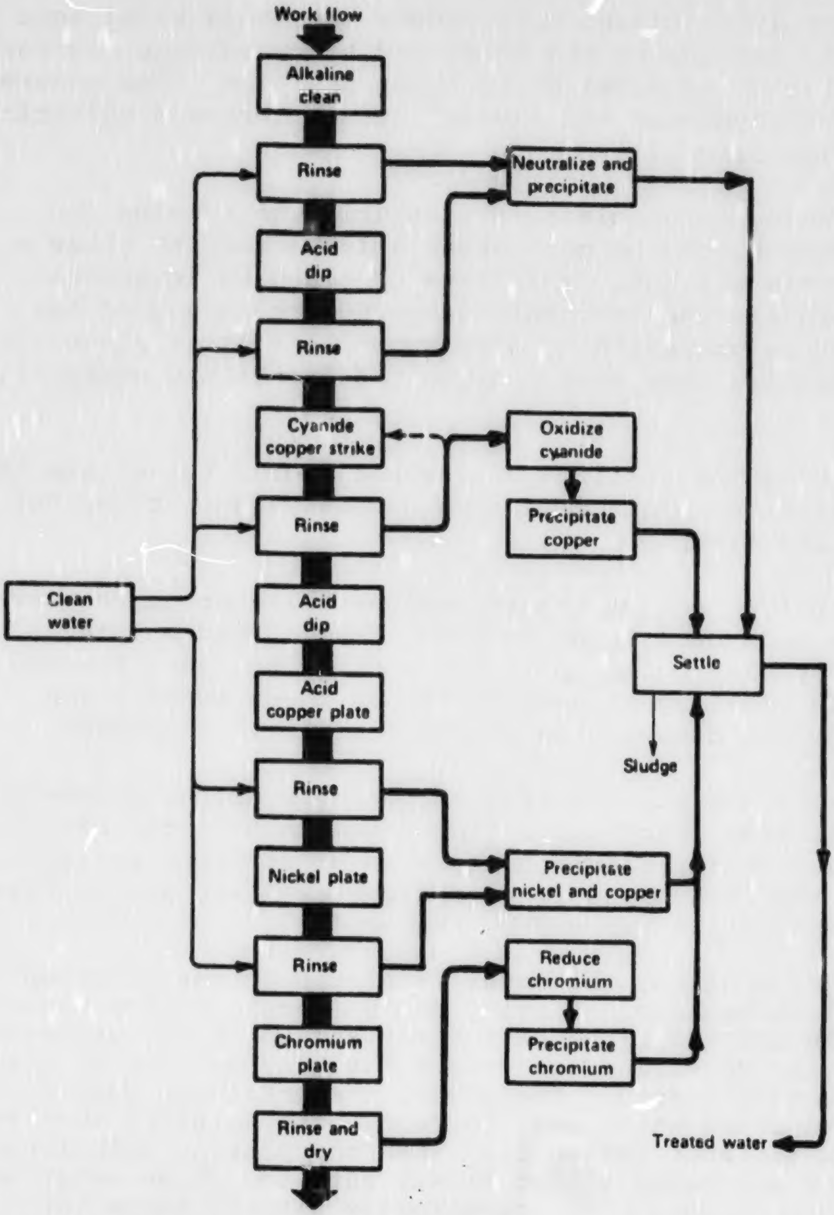
Electroplating (A) (B) (C)

The electroplating process includes pretreatment steps such as cleaning, electroplating, rinsing, and drying. The cleaning operation consists of two or more steps that are required for removing grease, oil, soil, and oxide films from the basis metal surface in order to insure good electroplating adhesion. In the electroplating process, a solution containing metal ions is reduced or plated onto a cathode surface, which is the material being plated. The metal ions in solution are replenished by the dissolution of metal from bars, wire or baskets that are used as the plating material and act as the anode. Metal ions can also be replaced by adding metal salts directly into the plating solution. In this case an inert material must be selected for the anode. Hundreds of different electroplating solutions have been adopted commercially. However, only two or three types are utilized widely for a single metal or alloy.

Parts can either be barrel plated or rack plated. Barrel plating, used for small parts, consists of placing the parts in a rotating barrel, and allowing the parts to tumble freely. Rack plating consists of attaching the parts to a frame which dips the parts into the solution, and also carries the parts from one tank, or operation, to another. After the parts have been plated they are rinsed in order to remove the plating solution, and then dried. Rinsewaters are a major source of wastewater. Figure 8-9-1 is a flow diagram typical of the electroplating industry.

Cleaning involves the removal of oil, grease, and dirt from the surface of the basis material. Cleaning, or degreasing, may be accomplished in one of several ways: alkaline cleaning, electrolytic (anodic and cathodic) cleaning, diphase cleaning, emulsion cleaning, soaking, solvent cleaning, and ultrasonic cleaning.

Alkaline cleaners most widely used in preparing the basis material are composed of one or more of the following chemicals: sodium hydroxide, sodium carbonate, sodium metasilicate, sodium phosphate, sodium silicate, sodium tetraphosphate, and a wetting agent. Combinations and concentrations of these chemicals vary depending on the basis material and the type of soil being cleaned. Wastes contain the cleaning solution plus the dirt removed from the basis material.


Work flow
Alkaline clean
Rinse
Neutralize and precipitate
Acid dip
Rinse
Cyanide copper strike
Oxidize cyanide
Rinse
Precipitate copper
Clean water
Acid dip
Settle
Acid copper plate
Sludge
Rinse
Nickel plate
Precipitate nickel and copper
Rinse
Reduce chromium
Chromium plate
Precipitate chromium
Rinse and dry
Treated water

SCHEMATIC FLOW CHART FOR WATER FLOW IN CHROMIUM PLATING ZINC DIE CASTINGS, DECORATIVE

Figure 8-9-1
Electroplating

In the electrolytic cleaning procedure the basis metal acts as either the cathode or the anode and a low voltage current is passed through an alkaline cleaning solution. The generation of gases (hydrogen and oxygen) cause increased agitation enhancing dirt removal.

Diphase cleaning takes place in a solution containing two layers or phases, one being a water soluble and the other a water insoluble solvent. This type of cleaning is useful when both organic and inorganic compounds are required for cleaning. This operation is also known as solvent cleaning. Emulsion cleaning uses water, organic solvents and emulsifying agents.

Ultrasonic cleaning utilizes ultrasonic energy to agitate the cleaning solution. This is a more expensive operation, but saves time and labor.

During the production of metals, oxides build up on the surface during such operations as heat treating and welding. Also rust may have built up if the part is not used immediately. Acid pickling is used to remove these oxide films and involves the dissolution of oxide scale in the acid.

Acid solutions are made up from one or more of the following acids: sulfuric, phosphoric, fluoboric, chromic and nitric acids. The pickling solution needs to be replaced periodically, and the spent acid is discharged as waste and contains the acids and metals removed by the acids.

Following preparation, the metal is plated by the electroplating or electroless methods. Plating baths contain a wide variety of chemicals and additives, which may end up in the wastewater. Electroplating solutions are reused for long periods of time and are infrequently dumped. Therefore, the principal source of waste is the rinse water used to remove the solution that remains on the work surfaces (dragout). When the plating solutions are wasted, they are usually bled slowly into the rinse water waste stream. On the other hand, electroless plating baths may periodically be discharged since the life of these baths are shorter than for electroplating baths.

Copper is electroplated from four (4) types of baths: alkaline cyanide, acid sulfate, pyrophosphate, and fluoborate, which are prepared with a corresponding copper salt. Copper is extensively electroplated as a base for further electroplating with nickel and chromium.

Nickel is electroplated from Watts (sulfate-chloride-boric acid), sulfamate, chloride, and fluoborate baths. Each type of solution is prepared with the corresponding nickel salt, a buffer and a small concentration of wetting agent.

In many operations nickel plating is followed by chrome plating.

All chromium plating solutions contain chromic acid and a small amount of sulfuric acid or a mixture of sulfuric acid and fluosilicate or fluoride ions. Spray carried from the solution by the gases generated at electrode surfaces is a significant waste source. Air scrubbers can recover and recycle it to the chromium bath.

Zinc is electroplated in cyanide solutions containing sodium cyanide, zinc oxide or cyanide and sodium hydrozide; non-cyanide alkaline solutions prepared with a variety of chelating agents; acid or neutral chloride baths. Zinc waste is generated during continuous or batch filtration. Gas evolution at electrode surfaces create aerosol particles which can be removed by water scrubbing.

Silver and gold are plated from cyanide baths. Since both metals are costly, much effort is made to recover them from waste streams, so that the major pollutant load is cyanide.

Platinum, rhodium, palladium, iridium, and ruthenium are used much less frequently than those previously mentioned. In addition, very little, if any, waste is expected from these operations. This is due to the fact that very small volumes of baths are used, and extensive recovery techniques are employed.

Specialty metals operations exist in only a few places in the country, and are associated with large industrial complexes, such as the aerospace industry. Therefore, a specialty metal plating shop cannot be identified as such, but will be part of an overall process in other industries.

As much as 90% of the water usage in this industry is from rinsing. The rinse water is used to remove the films of processing solutions (plating solutions) from the surface of the plated materials. In performing this task, the water becomes contaminated with the constituents of the operating solutions, and is discharged as a pollutant bearing stream. Many plants use more rinse water than is required, and in these cases water volume should be reduced.

Electroless plating is used when a thicker coat of metal is required than can be accomplished by electrolytic plating described above. Electroless is also used to coat complex shaped items and to plate plastic parts. Nickel and copper are the primary coating materials used in this process.

Electroless plating occurs by catalysis rather than by interchange of ions as in electroplating, and electricity is not used, as the name implies. Some materials are conditioned to attract the coating materials, while others accept the coating without conditioning.

There are a variety of preparation steps prior to electroless plating. Parts are cleaned in the same manner as in electroplating (e.g. alkaline cleaning). Plastics are prepared by roughening the surface by abrasion or by chemical means with chromic acid. Plastic parts are conditioned by placing them in a solution of stannous chloride. Iron, nickel, and cobalt do not require conditioning steps prior to plating, but do require cleaning; while aluminum and magnesium do require conditioning steps in addition to cleaning.

The electroless baths used for coating nickel are acidic, and contain nickel chloride or sulfate, sodium hypophosphate as the reducing agent, and an organic acid. The organic acid acts as both a buffer to help maintain the pH of the bath and as a complexing agent for the nickel ions in solution. Copper baths contain copper sulfate with either Rochelle salt (sodium potassium tartrate) or EDTA (ethylenediaminetetraacetic acid, sodium salt) as the complexing agent and formaldehyde as the reducing agent. Unlike conventional electroplating solutions which are commonly used for many years and are seldom discarded, electroless plating baths have finite life and must be periodically discarded as waste. The baths are usually trickled slowly into a rinse tank, which acts as a diluting step.

Coating operations can be a complete operation performed by a metal finishing shop, and are then classified as "coatings" plants (subcategory-E). However chemical conversion coating operations can also be a post treatment operation in an electroplating plant, and would then fall under subcategory-A. Refer to the process description given for subcategory (E) for more information on this process.

Metal coloring consists of converting the metal surface to its oxide form, or to an insoluble metal compound by immersing the metal in an aqueous solution. These finishes are used on copper, steel, zinc, and cadmium. Because the coatings are extremely thin and delicate, and lack resistance to handling and the atmosphere, they are given a coat of clear lacquer to protect the colored metal surface. Organic dyes can also be added to the coloring solution to impart a particular color desired. Wastewater production is similar to electroplating processes.

Anodizing (D)

The anodizing process is an electrolytic oxidation process by which the surface of the metal is converted to an insoluble oxide having desirable properties. Anodizing provides corrosion protection, decorative surfaces, a base for painting and other coating operations, and special electrical and engineering properties. Aluminum, zinc and magnesium are the metals which are anodized, but aluminum is the major material treated by this process.

The metal is prepared by soak cleaning with an alkaline cleaner or a phosphoric acid solution. Cleaning etches the metal slightly, which insures an active surface for anodizing. The metal is then immersed in sulfuric and chromic acid solutions followed by rinsing. Wastes are similar to those generated by electroplating rinse water.

Anodizing posttreatment for aluminum consists of improving the corrosion resistance of the coatings by immersing the material in deionized water at a temperature of 99°C (210°F). Sometimes organic dye is added to impart coloring. Wastewaters from this operation should not be high in pollutant loading unless organic dyes are used.

Chemical Conversion Coatings (E)

Protective coatings or films are produced on metal surfaces by chromating, phosphating or immersion plating.

Chromating - A portion of the base metal is converted to one of the components of the film by reaction with aqueous solutions containing hexavalent chromium and other active organic or inorganic compounds. Chromate coatings are most frequently applied to the following metals: zinc, cadmium, aluminum, magnesium, copper, brass, bronze, and silver. The coatings can be applied by either electrochemical action or chemical immersion. These coatings are used for protective or decorative purposes or as a base for paint when the original material does not have good adhering properties for paint. Chromate conversion coatings are frequently applied to zinc or cadmium plated parts immediately following electrodeposition. The wastewaters are similar to those for electroplating processes.

Phosphating - Phosphating is the treatment of iron, steel, zinc plated steel, and other metals by immersion in a dilute solution of phosphoric acid plus other reagents to produce an integral conversion coating on the surface. The process is similar to chromating, and the wastes are similar to electroplating waste streams.

Immersion Plating - This is a chemical plating process in which a thin metal deposit is obtained by chemical displacement of the basis material. In immersion plating a metal will displace from solution any other metal that is below it in the electromotive series of elements. The less active metal will be deposited from solution while the more active metal (the item being plated) will be dissolved. This process is used to insure corrosion protection or as a preparation for painting or rubber bonding, and is mostly used for the following combinations:

1. Tin on brass, copper, steel or aluminum.
2. Copper on steel.
3. Gold on copper or brass.
4. Nickel on steel.

Preparation for immersion plating consists of an alkaline cleaning step and a pickling step, which produce wastewaters similar to the pretreatment steps described earlier.

Chemical Milling and Etching (F)

Chemical milling is the process of shaping, machining, fabricating or blanking metal parts to specific design configurations and tolerances by controlled dissolution with chemical reagents or etchants. Chemical etching is the process of removing relatively small amounts of metal from the surface to improve the surface condition of the basis metal or to produce a pattern such as printed circuit boards. Grease and dirt are removed from metal surfaces by vapor degreasing and alkaline cleaning, and scale and films are then removed by pickling. Areas where no metal removal is desired are masked off by dipping, spraying or roll or flow-coating. Mask patterns can also be applied by the use of photosensitive resists, which are used for printed circuits. After the masking step, the part is given an acid dip to activate the surface for etching. Etching solutions include ferric chloride, nitric acid, chromic acid, sodium and ammonium persulfate, and cupric chloride. Wastewaters contain the etching solutions plus concentrations of the particular metal being etched.

4. Wastewater Characterization

Table 8-9-1 shows wastewater characteristics for the industry. Sources of wastewater include:

1. Rinsing to remove films of processing solution from the surface of the work pieces at the site of each operation.

TABLE 8-9-1

METAL FINISHING INDUSTRY

Raw Wastewater Characteristics[1]

Parameter	Concentration, mg/l
Flow, gpd	10 M - 500 M
Flow Type	C or I
TSS	5-20
TDS	500-1 M
pH	2*-13*
Zinc	10*-100*
Iron	10-1000
Cadmium	10*-100*
Nickel	10*-100*
Copper	10*-100*
Lead	10*-100*
Sodium	500
Aluminum	0[2]
Chromium, Hexavalent	8*-40[3]*
Chromium, Total	10*-50[4]*
Cyanide	20*-100*
Fluoride	5-500*
Phosphate	5-500

Notes:
1 Data obtained from EPA files
2 Anodizing wastes can have aluminum concentrations between 50-100 mg/l
3 Range shown is after dilution with other streams. Without dilution, 150-400 mg/l
4 Range shown is after dilution with other streams. Without dilution, 200-500 mg/l
M = 1,000
C - Continuous
I - Intermittent
* See Appendix 5 for parameters which may be inhibitory to biological systems.

2. Spills and leaks.
3. Air pollution scrubbers.
4. Dumping of plating solutions.
5. Washing of equipment.
6. Discharges of cooling water.

5. Control and Treatment Technology

In-Plant Control - The control of electroplating wastewaters includes process modifications, material substitutions, good housekeeping and water conservation techniques including:

a. Elimination of copper plating by increasing the thickness of nickel.
b. Substituion of dilute electroplating solutions for concentrated baths where possible.
c. Substituion of noncyanide solutions in place of cyanide solutions, where possible.
d. Substitution of trivalent chromium baths for hexavalent chromium baths.
e. Improvement in the racking procedure to improve drainage from surfaces over the process tank prior to rinsing.
f. Increasing drainage time over process tank.
g. Reducing viscosity of the process solution.
h. Addition of wetting agent to process solution to reduce surface tension.
i. Installation of air or ultrasonic agitation.
j. Installation of counterflow rinses whereby water exiting the last tank in the rinsing operation becomes the feed water for the preceding rinse. This practice can reduce water consumption by as much as 90%.
k. Minimizing water use.

Treatment Technology - The first step in treating metal finishing wastewaters is to separate the cyanide bearing waste streams from the chromium bearing waste streams. Then, wastewater containing only metals should be segregated as a third waste stream. Cyanide is generally destroyed by oxidation under alkaline conditions with chlorine. The reactions take place in baffled tanks with adequate detention times for the destruction to proceed to completion. Since hexavalent chromium is soluble, it must be reduced to the trivalent form before it can be precipitated. This is usually accomplished under acidic conditions with sulfur dioxide, sodium bisulfite or ferrous sulfate. The chemical reactions are also generally accomplished in baffled tanks. After the cyanide is destroyed and the chromium is reduced, these streams can then be combined with the metal bearing streams for precipitation and removal of the metals.

Table 8-9-3 contains wastewater treatment practices for this industry.

TABLE 8-9-3

METAL FINISHING INDUSTRY WASTEWATER TREATMENT PRACTICES

Pollutant and Method	Effluent Levels Attainable, Mg/L
Heavy Metals	
Precipitation, Floculation and Clarification	
Iron	1.0
Zinc	0.5
Copper	0.5
Nickel	0.5
Lead	0.5
Tin	1.0
Cadmium	0.3
Cyanide	
Cyanide destroyed to carbon dioxide and nitrogen	.05-0.5
Chrome	
Hexavalent chrome reduction to trivalent chrome, plus precipitation and clarification	0.5

1. General Industry Description

Organic chemicals are the raw materials for a multitude of products the public uses daily, including plastics, synthetic fibers, synthetic rubber, dyes, solvents, food additives, pharmaceuticals, lubricants, detergents, and cosmetics. Synthetic organic chemicals are derived as a result of the physical and chemical conversion operations from naturally occurring raw materials such as petroleum, natural gas, and coal.

Approximately 50% of the plants in this industry discharge to municipal treatment works. Wastewaters from this industry contain BOD, COD, TSS, phenols, sulfates, oil and grease, and some metals.

Establishments engaged in this industry are covered by Standard Industrial Classification (SIC) 286.

2. Industrial Categorization

This industry has been divided into the following subcategories; each includes a series of products as follows:

Subcategory	Products	Designation
Nonaqueous Processes	Benzene-Toluene-Xylene (BTX) Cyclohexane Vinyl Chloride Cumene P-Xylene	A
Processes with Process Water Contact as Steam Diluent or Absorbent	Acetone Butadiene Ethyl Benzene Ethylene and Propylene Ethylene Dichloride Ethylene Oxide Formaldehyde Methanol Methyl Amines Vinyl Acetate Vinyl Chloride Acetaldehyde Acetylene Butadiene Styrene	B

Subcategory	Products	Designation
Diluent or Absorbent (Continued)	Chlorobenzene	
	Chloromethanes	
	Chlorotoluene	
	Diphenylamine	
	Perchloroethylene	
	Phthalic anhydride	
	Hexamethylenediamine	
	Methyl ethyl ketone	
	Tricresyl phosphate	
	Adiponitrile	
	Benzoic acid and benzaldehyde	
	Methyl Chloride	
	Maleic anhydride	
Aqueous Liquid Phase Reaction Systems	Acetic acid	C
	Acrylic acid	
	Coal tar	
	Ethylene glycol	
	Terephthalic acid	
	Acetaldehyde	
	Caprolactam	
	Coal tar	
	Oxo chemicals	
	Phenol and acetone	
	Aniline	
	Bisphenol A	
	Dimethyl terephthalate	
	Acrylates	
	p-Cresol	
	Methyl methacrylate	
	Tetraethyl lead	
	Ethyl acetate	
	Propyl acetate	
	Propylene glycol	
	Cyclohexanone oxime	
	Isopropanol	
	Oxalic acid	
	Formic acid	
	Calcium stearatic	
	Hexamethylenetetramine	
	Hydrazine solutions	
	Isobutylene	

Subcategory	Products	Designation
Aqueous Liquid Phase Reaction Systems (Continued	Sec-bentyl alcohol	
	Acrylonitrile	
	Synthetic cresol	
	Caprolactam	
	p-Aminophenol	
	Propylene Oxide	
	Pentaerythritol	
	Saccharin	
Batch and Semi-Continuous Processes	o-Nitroaniline	D
	p-Nitroaniline	
	Pentachlorophenol	
	Fatty acids	
	Fatty acid derivatives	
	Ionone and methylionone	
	Methyl salicylate	
	Miscellaneous batch chemicals	
	Citronellol and Geraniol	
	Plasticizers	
	Dyes and dye intermediates	
	Pigments, toners	
	Pigments, lakes	
	Citric acid	
	Napthtenic acid	
	Sodium glutamate	
	Tannic acid	
	Vanillin	

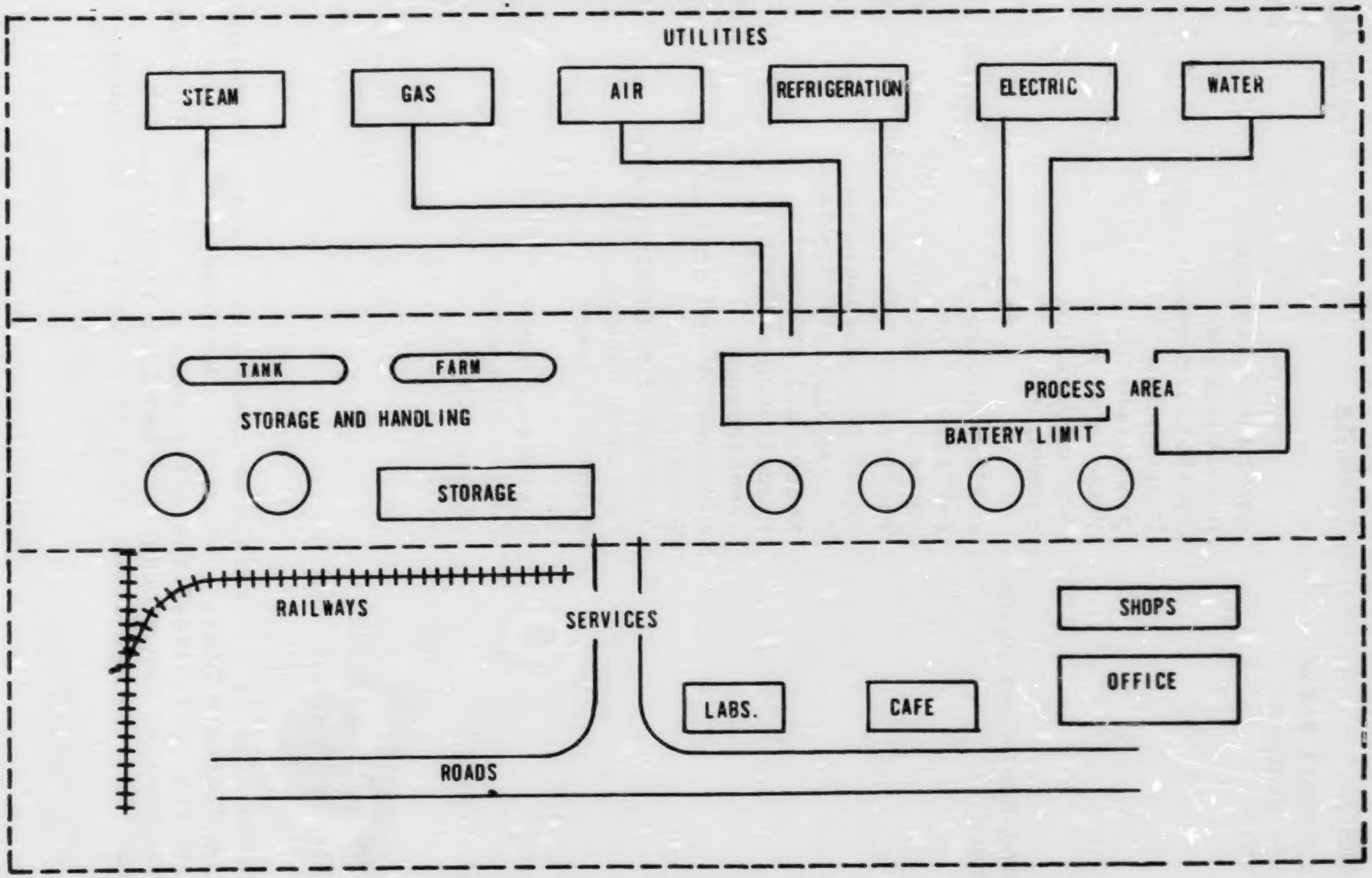
3. Process Description

General

The process area of an organic manufacturing plant is referred to as the "Battery Limit", while the remainder of the plant is called the "Off-Sites".The off-sites can be broken down into their components; the storage and handling facilities, the utilities, and the services. This is illustrated in Figure 8-10-1.

FIGURE 8-10-1

PLOT PLAN FOR CHEMICAL PLANT
ILLUSTRATING FOUR-AREA LAYOUT


UTILITIES
STEAM
GAS
AIR
REFRIGERATION
ELECTRIC
WATER
TANK
FARM
STORAGE AND HANDLING
STORAGE
PROCESS AREA
BATTERY LIMIT
RAILWAYS
SERVICES
SHOPS
OFFICE
LABS.
CAFE
ROADS

The storage facilities associated with any chemical plant depend upon the physical state (i.e. solid, liquid, or gas) of the feedstocks and products. Storage equipment includes cone-roof tanks for liquids, cylindrical or spherical tanks for gases, and concrete pads or silos for solids. Wastewater emanating from this part of the plant normally results from storm run-off, tank washing, accidental spills, and aqueous bottoms periodically drawn from storage tanks. These wastes are generally small in volume, but since they do come into contact with process chemicals, these chemicals will appear in the waste stream.

Utility functions such as the supply of steam and cooling water generally are set up to service several processes. Noncontact steam, generated in the boiler house, is circulated through a closed loop whereby varying quantities are made available to the different processes.

The uses for steam are as follows:

a. For noncontact process heating.
b. For power generation such as steam driven turbines, compressors, and pumps.
c. For use as a diluent, stripping medium, or source of vacuum. This use of steam will become contaminated and will need treatment.

Wastes from non-contact use of steam come from purges of the system, boiler blowdowns, and water treatment systems which are used to make good quality water for the steam generation system. Non-contact cooling water is also supplied to the processes. Once through cooling systems constitute an uncontaminated waste stream, while cooling tower blowdowns from closed cooling systems contain water treatment chemicals.

The service area of the plant contains the buildings, shops, and laboratories, in which the personnel work. Waste streams are generated from laundry facilities, sanitary facilities, and wastes from laboratory and shop operations.

In regard to the "battery limits", most plants manufacture many different products. Each process is itself a series of unit operations which causes chemical and physical changes in the feedstock or products. In the commercial synthesis of a single product from a single feedstock, there generally are sections of the process associated with: the preparation of the feedstock; the chemical reaction; the separation of reaction products; and the final purification of the desired product. Each unit operation may have drastically different water usages associated with it. The type and quantity of contact waste water are therefore directly related to the nature of the various processes. This in turn implies that the types and quantities of waste water generated by each plant's total production mix are unique.

The production from a given process module is related to the design capacities of the individual unit operations within it. In many cases, the unit operations are arranged as a single train in series. In other cases, some unit operations such as the reaction are carried in several small reactors operating in parallel.

The flow of material between unit operations within a process may be either a continuous stream or through a series of batch transfers.

There are two major types of manufacturing process within the industry:

a. Continous processing operations.
b. Batch processing operations.

Facilities utilizing continuous processes manufacture products in much greater volumes than do batch operations. Although the initial manufacture of many chemicals was first done by batch processing, changes to continuous processing were made when markets were enlarged to meet increasing and changing demands.

Batch processing is still extensively practiced, particularly when the production is small or where safety demands that small quantities be handled at one time. Furthermore, batch operations are more easily controlled when varying reaction rates and rapid temperature changes are key considerations.

The feed preparation section may contain equipment such as furnaces where the liquid feed is vaporized or heated to reaction temperature, or large steam driven compressors for compressing gaseous feed to the reaction pressure. It may contain distillation columns to separate undesired feed impurities which might damage the catalyst in the reactor or cause subsequent unwanted side reactions. Impurities may also be removed by preliminary chemical conversion (such as the hydrogenation of diolefins) or by physical means such as silica gel driers to remove trace amounts of moisture.

The reaction section of the process module is where the principal chemical conversions are accomplished. The reactor may be as simple as a hollow tube used for noncatalytic vapor-phase reactions. However, most industrial reactions are catalytic and generally require more complex reactor designs. The specific reactor design is usually governed by the required physical state of the reactants and catalyst.

Catalysts are of two types: heterogeneous and homogeneous. Heterogeneous catalysts are usually solids which may be composed of chemically inactive material such as finely ground aluminum or contain metals such as cobalt, platinum, iron, or manganese which are impregnated on a solid support. In heterogeneous reaction systems, the reactants are usually in the vapor phase. The conversion proceeds in three steps: adsorption of the reactants upon the surface of the catalyst; chemical reactions on the surface of the catalyst; and desorption of the products from the catalyst surface.

Homogeneous catalysts exist in the same physical state as the reactants and products. This may require the use of an aqueous or non-aqueous solvent to provide a reaction media. Typical homogeneous catalysts include strong acids, bases, and metallic salts which may be in the form of a solution or a slurry. It should be noted that the recovery, reconcentration, or regeneration of these catalysts may require the use of processing equipment much more elaborate than the reactor itself.

The recovery of reaction products may involve a wide variety of processing operations. If the reactor effluent is a vapor, it may be necessary to condense and quench the products in a direct contact medium such as water. In many instances, the desired products are absorbed in water and are subsequently stripped from the water by heating. Liquid reactor effluents are separated from solvents (and catalysts) by distillation. In almost all cases, the conversion of feed is not complete, so that continuous separation and recycle of unconverted feed to the reactor is necessary.

Final purification of the products is normally required both when they are to be sold and when they are used as intermediates. Most specifications restrict contaminant levels to the range of parts per million. Because of this, additional operations such as distillation, extraction, crystallization, etc. are necessary. The product is pumped from the battery limits to tanks in the storage area.

In large-scale continuous processes, all of the subsections of the process module are operated with the use of automated controls; in some cases, complete automation or computer control is utilized.

When chemical manufacturing is on a small scale, or when it is not adaptable to continuous procedures, a batch sequence is frequently used. This requires more supervision on the part of operators and engineers, because the conditions and procedures usually change from the start to the finish. Batch operations with small production and variable products also transfer equipment from the making of one chemical to that of another based on the same type of chemical conversion. Hundreds of specific products may be manufactured within the same building.

This type of processing requires the cleanout of reactors and other equipment after each batch. Purity specifications may also require extensive purging of the associated piping. Rapid changes in temperature during the batch sequence may also require the direct addition of ice or quench water as opposed to slower non-contact cooling through a jacket or coils.

Process waters from batch or continuous processes within the battery limits include not only water produced or required by the chemical reactions but also any water which comes in contact with chemicals within each of the process modules. Although the flows associated with these sources are generally much smaller than those from non-contact sources, the organic pollution load carried by these streams is greater by many orders of magnitude.

Process water is defined as all water which comes in contact with chemicals within the process and includes:

1. Water required or produced (in stoichiometric quantities) in the chemical reaction.

2. Water used as a solvent or as an aqueous medium for the reactions.

3. Water which enters the process with any of the reactants or which is used as a diluent (including steam).

4. Water associated with the catalyst system, either during the reaction or during catalyst regeneration.

5. Water used as an absorbent or as a scrubbing medium for separating certain chemicals from the reaction mixture.

6. Water introduced as steam to strip certain chemicals from the reaction mixture.

7. Water used to wash, remove, or separate chemicals from the reaction mixture.

8. Water associated with mechanical devices such as steam-jet ejectors for drawing a vacuum on the process.

9. Water used as a quench or direct contact coolant such as in a barometric condenser.

10. Water used to clean or purge equipment used in batch type operations.

11. Runoff or wash water associated with battery limits process areas.

The type and quantity of process water usage are related to the specific unit operations and chemical conversions within a process. The term "unit operations" is defined to mean specific physical separations such as distillation, solvent extraction, crystallization, adsorption, etc. The term "chemical conversion" is defined to mean specific reactions such as oxidation, halogenation, neutralization, etc.

Description of Subcategories

Four process subcategories have been established. Subcategories A, B, and C relate to continuous processes, while Subcategory D relates to batch processes. The subcategories are described as follows:

Nonaqueous Processes (A)

In this subcategory there is minimal contact between water and reactants or products within the process. Water is not required as a reactant or diluent and is not formed as a reaction product. The only water usage stems from periodic washes of working fluids or catalyst hydration. Raw waste loads should approach zero with the only variations caused by spills or process upsets.

Processes With Process Water Contact as Steam Diluent or Absorbent (B)

Process water usage is in the form of dilution steam, a direct contact quench, or as an absorbent for reactor effluent gases. Reactions are all vapor-phase and are carried out over solid catalysts. Most processes have an absorber coupled with steam stripping of chemicals for purification and recycle. Steam is also used for de-coking of catalyst.

Continuous Liquid-Phase Reaction Systems (C)

Liquid-phase reactions where the catalyst is in an aqueous medium such as dissolved or emulsified mineral salt, or acid-caustic solution. Continuous regeneration of catalyst system requires extensive water usage. Substantial removal of spent inorganic salt by-products may also be required. Working aqueous catalyst solution is normally corrosive. Additional water may be required in final purification or neutralization of products.

Batch and Semicontinuous Processes (D)

Processes are carried out in reaction kettles equipped with agitators, scrapers, reflux condensers, etc. depending on the nature of the operation. Many reactions are liquid-phase with aqueous catalyst systems. Reactants and products are transferred from one piece of equipment to another by gravity flow, pumping, or pressurization with air or inert gas. Much of the material handling is manual with limited use of automatic process control. Filter presses and centrifuges are commonly used to separate solid products from liquid. Where drying is required, air or vacuum ovens are used. Cleaning of noncontinuous production equipment constitutes a major source of waste water. Waste loads from product separation and purification will be at least ten times those from continuous processes.

4. Wastewater Characterization

Table 8-10-1 contains raw wastewater characteristics for the industry. The raw waste loads shown in the table for subcategories A, B, C are based on contact process water only. Non-contact water is excluded for continuous processes since these plants have been able to achieve segregation of non-contact cooling water or steam. Subcategory D includes all water usage associated with the process in that rapid cooling with direct contact is required in the manufacture of dyes.

TABLE 8-10-1

ORGANIC CHEMICALS INDUSTRY

RAW WASTEWATER CHARACTERISTICS

	Subcategories			
Waste Parameter	Non Aqueous Processes-A	Processes with Process Water as Steam Diluent or Absorbent - B	Aqueous Liquid Phase Reaction Systems - C	Batch and Semi-continuous Processes - D
Flow Type	C	C	C	B
BOD (mg/l)		100-500		
TSS (mg/l)	10-100	10-2300	10-4M	20-4M
TDS (mg/l)	20-50M*	400-100M*	23-100M*	40-300M*
COD (mg/l)	100-10M*	200-5M*	10M-50M*	1M-10M*
Cyanide (mg/l)	0-1	0-0.3	0-1	0.02
TOC (mg/l)	100-3M	100-2M	3M-5M	
Phenol (mg/l)	0-15	0-20	0-6000	0-150
Ammonia Nitrogen (mg/l)	1-150	1-50	0-1000	5-1000
Oil (mg/l)	10-250*	2-200*	0-1200*	10-4000*
Metals	Present	Present	Present	Present
Color				Present

Notes:
M = 1,000
* See Appendix 5 for parameters which may be inhibitory to biological systems
B-Batch Process
C-Continuous Process

5. Control and Treatment Technology

In-Plant Control

The following in-plant control measures are practiced in this industry:

1. Substitution of surface heat exchangers for contact cooling water used in barometric condensers.
2. Regeneration of contact process steam from contaminated condensate.
3. Substitution of vacuum pumps for steam jet ejectors.
4. Recycle of scrubber water.
5. Recovery of insoluble hydrocarbons.
6. Solvent extraction for recovery of phenols.

Treatment Technology

Biological treatment is the major treatment technology used in this industry. Both single stage and multiple stage plants are used, especially when phenol removal is required. Filtration is also used as a polishing step after biological treatment.

Activated carbon is becoming more evident as an alternate treatment scheme to biological treatment. Contact times of 22 - 660 minutes are required as opposed to 10-50 minutes for domestic waste. Pretreatment for suspended solids and oil removal is required to levels of at least 10 mg/l TSS and 50 mg/l of oil.

Equalization is also good practice before all forms of treatment schemes. Table 8-10-2 gives removal efficiencies for the treatment systems described above.

TABLE 8-10-2

ORGANIC CHEMICALS INDUSTRY

WASTEWATER TREATMENT PRACTICES

Pollutant and Method	Removal Efficiencies %
BOD	
Biological Treatment	93
Filtration (percentage is between inlet and outlet of filter)	17
Pretreatment plus activated carbon	90
COD	
Single Stage Biological Treatment	69
Multiple Stage Biological Treatment	74
Filtration (percentage is between inlet and outlet of filter)	20
Pretreatment plus activated carbon	69
TOC	
Single Stage Biological Treatment	60
Multiple Stage Biological Treatment	79
Filtration (percentage is between inlet and outlet of filter)	20
Pretreatment plus activated carbon	87

1. General Industry Description

The Inorganic Chemical Manufacturing Industry produces a wide range of chemicals that are fundamental to the U. S. economy. The manufacturing plants tend to be large and produce multiple products by application of basic, simple chemical reactions and/or physical separation techniques from ores or natural brines. Plants tend to be located near raw materials or sources of needed chemicals.

The wastewaters from this industry are generally low in BOD, and COD, but do contain dissolved solids, alkalinity, suspended solids, and some metals. This industry includes Standard Industrial Classifications (SIC) 2812 and 2819.

2. Industrial Categorization

The major inorganic products segment of this industry has been divided into the following subcategories:

Subcategory	Designation
Aluminum Chloride	A
Aluminum Sulfate	B
Calcium Carbide	C
Calcium Chloride	D
Calcium Oxide and Calcium Hydroxide	E
Chlorine and Sodium or Potassium Hydroxide	F
Mercury Cell Process	F(a)
Diaphragm Cell Process	F(b)
Hydrochloric Acid	G
Hydrofluoric Acid	H
Hydrogen Peroxide	I
Oxidation of Alkyl Hydroanthroquinones	I(a)
Electrolytic Process	I(b)
Nitric Acid	J
Potassium Metal	K
Potassium Dichromate	L
Potassium Sulfate	M
Sodium Bicarbonate	N
Sodium Carbonate	O

Subcategory	Designation
Sodium Chloride	P
Solar Evaporation	P(a)
Solution Brine-Mining	P(b)
Sodium Dichromate and Sodium Sulfate	Q
Sodium Metal	R
Sodium Silicate	S
Sodium Sulfite	T
Sulfuric Acid	U
Titanium Dioxide	V
Chlorine Process	V(a)
Sulfate Process	V(b)

The significant inorganic products segment of this industry has been tentatively divided into the following subcategories:

1. aluminum fluoride
2. ammonium chloride
3. ammonium hydroxide
4. barium carbonate
5. borax
6. boric acid
7. bromine
8. calcium hydroxide
10. carbon dioxide
11. carbon monoxide
12. chrome green*
13. chrome yellow and orange*
14. chromic acid
15. chromic oxide*
16. copper sulfate
17. cuprous oxide
18. ferric chloride
19. ferrous sulfate
20. fluorine
21. hydrogen
22. hydrogen cyanide
23. iodine
24. iron blues*
25. lead oxide
26. lithium carbonate
27. manganese sulfate
28. molybdate chrome orange*
29. nickel sulfate
30. nitric acid (strong)
32. oxygen
33. potassium chloride
34. potassium iodide
35. potassium permanganate
36. silver nitrate
37. sidium bisulfite
38. sodium fluoride
39. sodium hydrosulfide
40. sodium hydrosulfite
41. sodium silicofluoride
42. sodium thiosulfate
43. stannic oxide
44. sulfur dioxide
45. zinc oxide
46. zinc sulfate
47. zinc yellow*

*Combined as chrome pigments and iron blues in one production subcategory.

3. Process Description

Aluminum Chloride (A)

Aluminum chloride is made by the reaction of chlorine with molten aluminum. The aluminum chloride vapor is collected on air cooled condensers. There are two sources of wastewater: uncondensed aluminum chloride and chlorine tail gases, and unreacted aluminum metal. If the tail gases are scrubbed, the aluminum chloride recovered, and the scrubbing solution returned to the system, no wastewater is produced in this process.

Aluminum Sulfate (B)

Aluminum sulfate is prepared by reaction in a digester of bauxite ore or aluminum clays with sulfuric acid. Figure 8-11-1 is a flow diagram for this process. The resulting product solution, containing muds and other insolubles from the ore, is then fed to a settling tank, wherein the insolubles are removed by settling and filtration. The aluminum sulfate may be sold as a solution or evaporated to yield a solid product.

Raw wastes from this process include insoluble muds from the digester, settling tank and filtration unit, as well as washwaters from vessel cleanouts. If spills and washwater are collected, and wastewater is treated and recycled, there is no discharge.

Calcium Carbide (C)

Calcium carbide is manufactured by the thermal reaction of calcium oxide and coke. Calcium oxide and dried coke are reacted in a furnace, and the product is then cooled, crushed, screened, packaged and shipped. The only wastes from the process are airborne dusts from the furnace, coke dryer and screening bag filters.

Calcium Chloride (D)

Calcium chloride is produced by extraction from natural brines. The salts are solution mined, and the resulting brine solution is concentrated. Chemicals are added to remove other materials such as sodium chloride, potassium, and magnesium salts. The

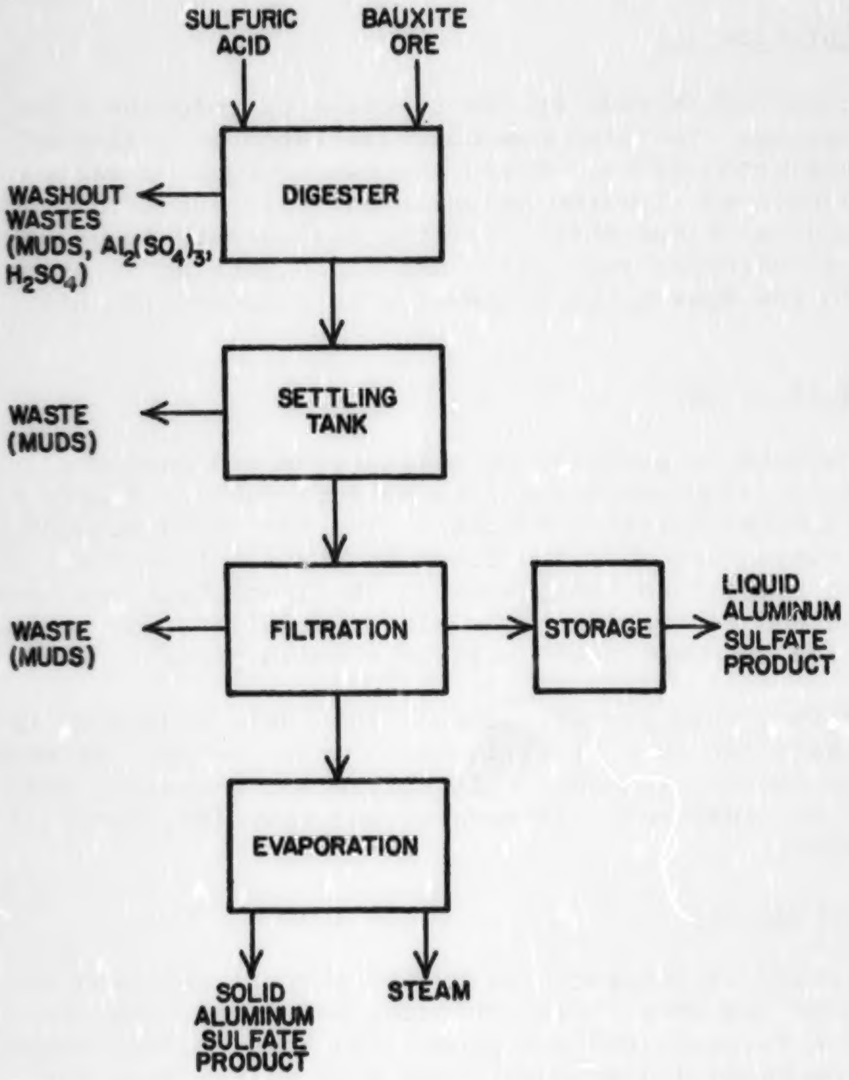

SULFURIC ACID
BAUXITE ORE
DIGESTER
WASHOUT WASTES (MUDS, $AL_2(SO_4)_3$, H_2SO_4)
SETTLING TANK
WASTE (MUDS)
FILTRATION
WASTE (MUDS)
STORAGE
LIQUID ALUMINUM SULFATE PRODUCT
EVAPORATION
SOLID ALUMINUM SULFATE PRODUCT
STEAM

FIGURE 8-11-1
STANDARD PROCESS DIAGRAM FOR ALUMINUM SULFATE MANUFACTURE (B)

remaining calcium chloride solution is evaporated to dryness, packaged, and sold. Raw wastes, consisting of weak brine solutions, come from blowdowns and from the partial evaporation steps used.

Calcium Oxide and Calcium Hydroxide (E)

Calcium oxide is manufactured by thermal decomposition of limestone in a kiln. The limestone is first crushed, then added to the kiln, where it is calcined to effect decomposition. The product is then removed from the kilns, marketed as calcium oxide, or slaked by reaction with water to produce calcium hydroxide. The only waste stream from this process is from the use of wet scrubbers for cleaning the plant gas effluent.

Chlorine and Sodium or Potassium Hydroxide (F)

Mercury Cell Process - F(a) Caustic and chlorine are produced from either sodium or potassium chloride raw materials depending on end product desired. Figure 8-11-2 shows a flow diagram for this process. The raw material is purified by dissolving in water followed by barium carbonate treatment to precipitate magnesium and calcium salts. The brine is then fed to the mercury cell, where the chlorine is liberated at one electrode and sodium-mercury amalgum is formed at the other. The chlorine is cooled, dried in a sulfuric acid stream, purified to remove chlorinated organics, compressed, and sold. The mercury-sodium amalgum is decomposed by water treatment in a "denuder" to form sodium (or potassium) hydroxide and hydrogen. These products are treated and sold, and the mercury recovered. The sulfuric acid stream is recycled.

Wastewaters consist of purification muds (calcium carbonate, magnesium hydroxide and barium sulfate) from brine purification, some spent brine solutions and condensates from chlorine and hydrogen compressions. Wastes also contain mercury.

Diaphragm Cell Process - F(b) The products and wastes of the diaphragm cell process are similar to those from the mercury cell process except that the cell is manufactured differently and mercury is not usually present in the effluent.

Hydrochloric Acid (G)

Hydrochloric acid is manufactured principally by two processes: (1) as a by-product of organic chlorinations; and (2) by direct

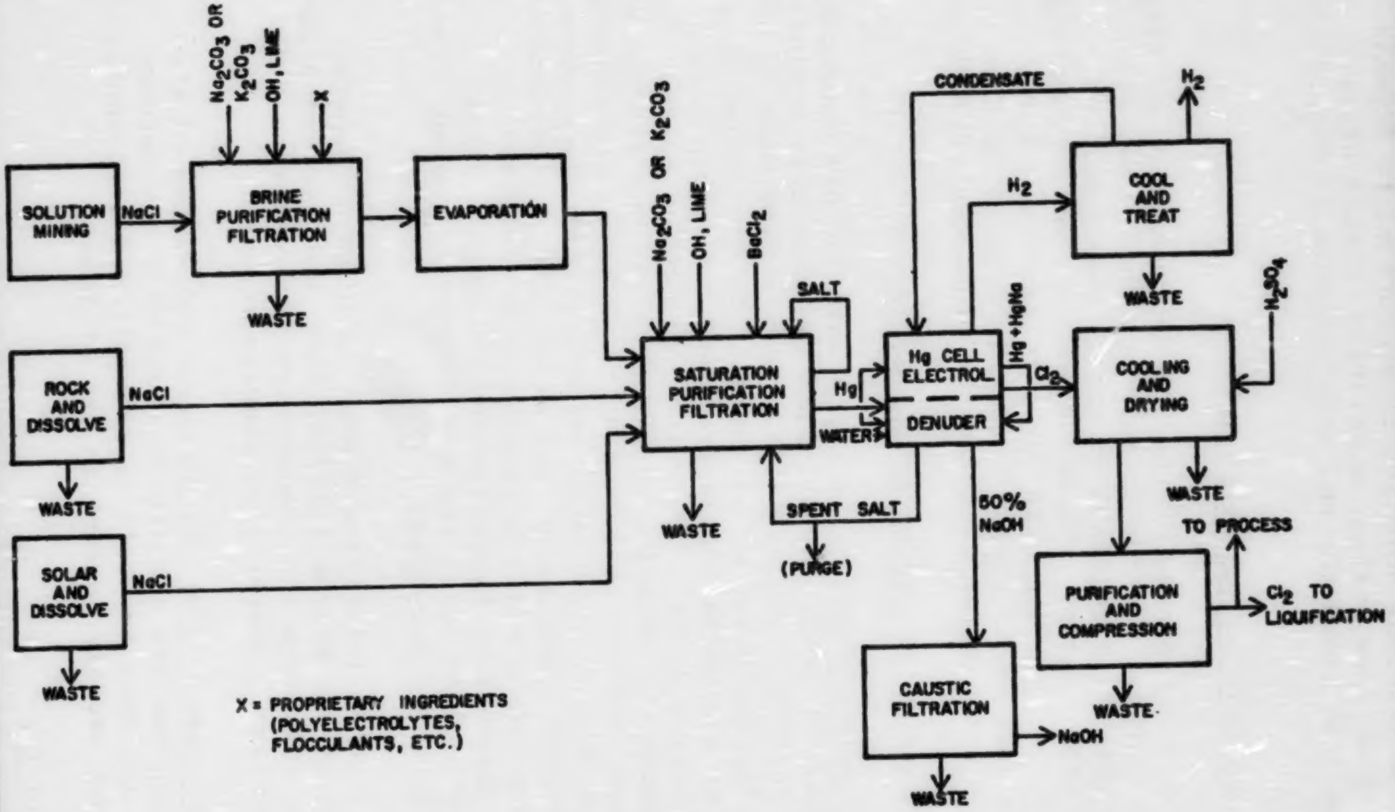

SOLUTION MINING
NaCl
Na_2CO_3 OR K_2CO_3
OH, LIME
X
BRINE PURIFICATION FILTRATION
WASTE
EVAPORATION
ROCK AND DISSOLVE
NaCl
WASTE
SOLAR AND DISSOLVE
NaCl
WASTE
Na_2CO_3 OR K_2CO_3
OH, LIME
$BaCl_2$
SALT
SATURATION PURIFICATION FILTRATION
WASTE
Hg
WATER
SPENT SALT
(PURGE)
CONDENSATE
Hg CELL ELECTROL.
DENUDER
Hg + HgNa
H_2
Cl_2
50% NaOH
COOL AND TREAT
H_2
WASTE
COOLING AND DRYING
H_2SO_4
WASTE
TO PROCESS
PURIFICATION AND COMPRESSION
Cl_2 TO LIQUIFICATION
WASTE
CAUSTIC FILTRATION
NaOH
WASTE
X = PROPRIETARY INGREDIENTS (POLYELECTROLYTES, FLOCCULANTS, ETC.)

FIGURE 8 -11-2
STANDARD
CHLORINE-CAUSTIC FLOW DIAGRAM MERCURY CELL PROCESS (F-a)

reaction of chlorine with hydrogen. Only production by direct reaction of chlorine is considered herein. In this process, hydrogen and chlorine are reacted in a vertical burner. The hydrogen chloride formed is condensed in an absorber from which it flows to a storage unit for collection and sale.

Waterborne wastes are only produced during start-ups. At other times, no wastewater flow is produced.

Hydrofluoric Acid (H)

Hydrofluoric acid is manufactured by reaction of sulfuric acid with fluorspar ore (mainly calcium fluoride). The reaction mixture is heated and the hydrofluoric acid leaves the furnace as a gas, which is then cooled, condensed and sent to a purification unit. There the crude hydrofluoric acid is redistilled and either absorbed in water to yield aqueous hydrofluoric acid or compressed and bottled for sale as anhydrous hydrofluoric acid. Wastewaters are generated from furnace cleanups. These washwaters are composed of salt-containing slurry water and fluoride-containing air scrubbers.

Hydrogen Peroxide (I)

Hydrogen peroxide is manufactured by three different processes: (1) An electrolytic process; (2) An organic process involving the oxidation and reduction of anthraquinone; and (3) A by-product of acetone manufacture from isopropyl alcohol. In this study, only the first two processes are discussed.

Electrolytic Process I(a) In the organic process, anthraquinone (or an alkylanthraquinone) in an organic solvent is catalytically hydrogenated to yield a hydroanthraquinone. This material is then oxidized with oxygen or air back to anthraquinone, with hydrogen peroxide being produced as a by-product. The peroxide is water-extracted from the reaction medium, and the organic solvent and anthraquinone are recycled. The recovered peroxide is then purified and shipped.

Electrolytic Process I(b) In the electrolytic process, a solution of ammonium bisulfate is electrolyzed. Hydrogen is liberated at the cathodes of the cells used, and ammonium persulfate is formed at the anode. The persulfate is then hydrolyzed to yield ammonium bisulfate and hydrogen peroxide which is separated from the solution by fractionation. The ammonium bisulfate solution is then recycled, and the peroxide is recovered for sale. Raw wastes consist of ammonium bisulfate losses, ion exchange losses, boiler blowdowns and some cyanide wastes from the special batteries used in electrolysis.

Wastewaters contain alkalinity, dissolved solids, and some metals (e.g. iron).

Nitric Acid (J)

Nitric acid is manufactured from ammonia by a catalytic oxidation process. Ammonia is first catalytically oxidized to nitric oxide, which is then further oxidized to nitrogen dioxide. The nitrogen dioxide is then reacted with water under pressure to yield nitric acid.

Wastewaters are produced only from cooling tower blowdown which contain water treatment chemicals.

Potassium Metal (K)

For the commercial preparation of potassium metal (K), potassium chloride is melted in a gas-fired melt pot and fed to an exchange column. The molten potassium chloride flows down over steel Raschig rings in the packed column, where it is contacted by ascending sodium vapors coming from a gas-fired reboiler. An equilibrium is established between the two, yielding sodium chloride and elemental potassium as the products. The sodium chloride formed is continuously withdrawn at the base of the apparatus and is normally sold. The column operating conditions may be varied to yield either pure potassium metal as an overhead product or to vaporize sodium along with the potassium to produce sodium potassium (NaK) alloys of varying compositions. Potassium metal of over 99.5 percent purity can be continuously produced by this process.

No process water is used in this process and no wastewater is produced.

Potassium Dichromate (L)

Potassium dichromate is prepared by reaction of potassium chloride with sodium dichromate. Potassium chloride is added to the dichromate solution, which is then pH-adjusted, saturated, filtered and vacuum cooled to precipitate crystalline potassium dichromate. The product is recovered by centrifugation, dried, sized and packaged. The mother liquor from the product centrifuge is then concentrated to precipitate sodium chloride which is removed as a solid waste from a salt centrifuge. The process liquid is recycled back to the initial reaction tank.

Only solid wastes and cooling water are produced in this process.

Potassium Sulfate (M)

The bulk of the potassium sulfate manufactured in the United States is prepared by reaction of potassium chloride with dissolved langbeinite ore (potassium sulfate-magnesium sulfate). The langbeinite ore is mined and crushed and then dissolved in water to which potassium chloride is added. Partial evaporation of the solution produces selective precipitation of potassium sulfate which is recovered by centrifugation or filtration from the brine liquor, dried and sold. The remaining brine liquor is either discharged to an evaporation pond, reused as process water or evaporated to dryness to recover magnesium chloride. The fate of the brine liquor is determined by the salability of the magnesium chloride by-product (depending on ore quality) and the cost of water to the plant.

The brine wastes that are produced contain primarily magnesium chloride. Much of the water is recycled.

Sodium Bicarbonate (N)

Sodium bicarbonate is manufactured by the reaction of soda ash (sodium carbonate) and carbon dioxide in solution. The product bicarbonate is separated by thickening and centrifugation and is then dried, purified and sold.

Wastewaters are produced from slurry thickener overflow which contain sodium bicarbonate and from power generation boiler foodwater purification.

Sodium Carbonate (O)

Soda ash (sodium carbonate) is produced by mining and by the Solvay Process. In the Solvay Process sodium chloride brine is purified to remove calcium and magnesium compounds. It is reacted with ammonia and carbon dioxide produced from limestone calcination to yield crude sodium bicarbonate which is recovered from the solutions by filtration. The bicarbonate is calcined to yield soda ash. The spent ammonia solution is reacted with slaked lime and distilled to recover ammonia values for process recycle. The calcium chloride formed as a by-product during the distillation is either discharged as a waste or recovered by evaporation.

Wastewaters are high in dissolved and suspended solids.

Sodium Chloride (P)

Sodium chloride is produced by three methods:

1. Solar evaporation of seawater;
2. Solution mining of natural brines;
3. Conventional mining of rock salt. (Not discussed here)

Solar Evaporation Process P(a) In the solar evaporation process, seawater is concentrated by evaporation in open ponds to yield a saturated brine solution. After saturation is reached, the brine is then fed to a crystallizer, wherein sodium chloride precipitates, leaving behind a concentrated brine solution (bittern) consisting of sodium, potassium and magnesium salts. The precipitated sodium chloride is recovered for sale and the brine is then further evaporated to recover additional sodium chloride values and is then either stored, discharged back to salt water or further worked to recover potassium and magnesium salts.

Solution Brine-mining Process P(b) In the solution brine-mining process, saturated brine for the production of evaporated salt is usually obtained by pumping water into an underground salt deposit and removing the saturated salt solution from an adjacent interconnected well, or from the same well by means of an annular pipe. Besides sodium chloride, the brine will contain some calcium sulfate, calcium chloride, magnesium chloride, and lesser amounts of other materials including iron salts and sulfides.

The chemical treatment given to brines varies from plant to plant depending on the impurities present. Typically, the brine is first aerated to remove hydrogen sulfide and, in many cases, small amounts of chlorine are added to complete sulfide removal and oxidize all iron salts present to the ferric state. The brine is then pumped to settling tanks where it is treated with soda ash and caustic soda to remove most of the calcium, magnesium and iron present as insoluble salts. After clarification to remove these insolubles, the brine is sent to multiple-effect evaporators. As water is removed, salt crystals form and are removed as a slurry. After screening to remove lumps, the slurry is washed, filtered, dried and screened.

Wastewaters are produced from boiler blowdowns, evaporator purges and cleanings, cooling waters and brine sludges.

Sodium Dichromate and Sodium Sulfate (Q)

Sodium dichromate is prepared by calcining a mixture of chrome ore ($FeO.Cr_2O_3$), soda ash and lime, followed by water leaching and acidification of the soluble chromates. The insoluble residue from the leaching operation is recycled to leach out additional material.

During the first acidification step, the pH of the chromate solution is adjusted to precipitate calcium salts. Further acidification converts chromate to the dichromate and a subsequent evaporation step crystallizes sodium sulfate (salt cake) out of the liquor. The sulfate is then dried and sold. The solutions remaining after sulfate removal are further evaporated to recover sodium dichromate. Chromic acid is produced from sodium dichromate by reaction with sulfuric acid. Sodium bisulfate is a by-product.

Wastewaters are generated from spills and washdowns, and contain hexavalent chromium. Boiler blowdown and water treatment processes can constitute other waste streams, which contain dissolved sulfates and chlorides.

Sodium Metal (R)

Sodium is manufactured by electrolysis of molten sodium chloride in a Downs electrolytic cell. After salt purification to remove calcium and magnesium salts and sulfates, the sodium chloride is dried and fed to the cell, where calcium chloride is added to give a low-melting $CaCl_2$-NaCl eutectic, which is then electrolyzed. Sodium is formed at one electrode, collected as a liquid, filtered and sold. The chlorine liberated at the other electrode is first dried with sulfuric acid and then purified, compressed, liquified and sold.

Wastewaters are produced from cleaning the electrolytic cells, cooling tower blowdowns, gas scrubbers, cooling waters, runoff water, and contain mostly dissolved chlorides.

Sodium Silicate (S)

Sodium silicate is manufactured by the reaction of soda ash or anhydrous sodium hydroxide with silica in a furnace, followed by dissolution of the product in water under pressure to prepare sodium silicate solutions. In some plants, the liquid silicate solutions are then further reacted with sodium hydroxide to manufacture metasilicates which are then isolated by evaporation and sold.

Wastewaters contain sodium silicate and unreacted silica.

Sodium Sulfite (T)

Sodium sulfite is manufactured by reaction of sulfur dioxide with soda ash. The crude sulfite formed in this reaction is then purified, filtered to remove insolubles from the purification step, crystallized, dried and shipped.

Wastewaters from the purification step contain sulfides, and vessel cleanouts contain sulfite and sulfate.

Sulfuric Acid (U)

Sulfuric acid is manufactured primarily by the contact process which involves catalytic oxidation of sulfur dioxide to sulfur trioxide and reaction of the sulfur trioxide with water to yield sulfuric acid. Within the contact process, there are three types of plants: double absorption, single absorption and spent acid.

In the double absorption contact process, sulfur is burned to yield sulfur dioxide which is then passed through a catalytic converter with air to produce sulfur trioxide. The sulfur trioxide is then absorbed in 95-97 percent sulfuric acid. The gases emerging from the absorber are fed to a second converter to oxidize the remaining sulfur dioxide to sulfur trioxide which is then absorbed in a second absorption tower. The tail gases are vented to the atmosphere; tail gas scrubbers are not required.

Process water is normally consumed or recycled. Cooling water is the only discharge.

The single absorption process differs from that previously described only in the arrangement of converters and absorbers. The rest of the process is the same. For the single absorption process, the sulfur dioxide is passed through one or more converters and then into one or more absorbers prior to venting to the atmosphere. This arrangement is less effective for both conversion of sulfur dioxide to sulfur trioxide and for absorption of the sulfur trioxide into the absorber sulfuric acid. As a result, the tail gases may have to be scrubbed to remove sulfur oxides, creating a waterborne waste not present for double absorption plants.

Spent acid plants use spent sulfuric acid in place of, or in addition to, sulfur as a raw material. While the acid production parts of these plants are the same as those for single absorption, these plants are unique because of the spent acid pyrolysis units used to convert the waste sulfuric acid raw materials to a sulfur dioxide feed stream. Discussion of wastes from spent acid plants is not included here.

Titanium Dioxide (V)

Titanium dioxide is the most widely used white pigment. It is produced by two methods: the "sulfate" process and the "chloride" process.

Chloride Process V(a) In the chloride process, shown in Figure 8-11-3, titanium dioxide (TiO_2) ores are chlorinated to produce titanium tetrachloride, iron chlorides and other metal chlorides. Coke is included to promote the reaction. The resulting titanium tetrachloride is oxidized to titanium dioxide and chlorine which is recycled.

Impurities in the system, including the iron and other metal chlorides, entrained coke and ore, carbon monoxide and dioxide, and hydrogen chloride all have to be removed prior to the oxidation reaction, creating a significant effluent waste control problem. After chlorination, the products are cooled

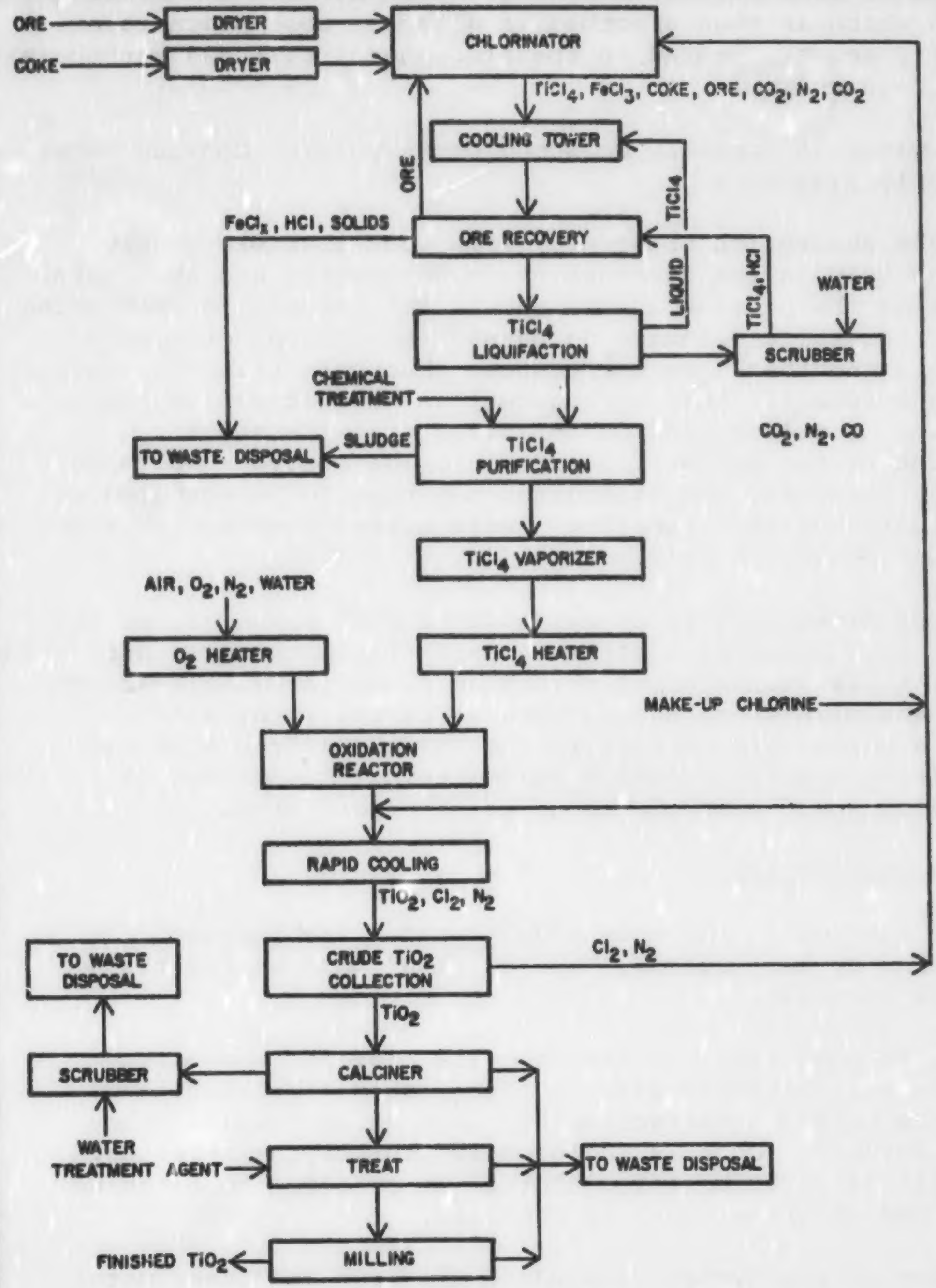

ORE
COKE
DRYER
DRYER
CHLORINATOR
TiCl4, FeCl3, COKE, ORE, CO2, N2, CO2
COOLING TOWER
ORE
TiCl4
FeClx, HCl, SOLIDS
ORE RECOVERY
LIQUID
TiCl4, HCl
WATER
TiCl4 LIQUIFACTION
SCRUBBER
CHEMICAL TREATMENT
CO2, N2, CO
TO WASTE DISPOSAL
SLUDGE
TiCl4 PURIFICATION
TiCl4 VAPORIZER
AIR, O2, N2, WATER
O2 HEATER
TiCl4 HEATER
MAKE-UP CHLORINE
OXIDATION REACTOR
RAPID COOLING
TiO2, Cl2, N2
TO WASTE DISPOSAL
CRUDE TiO2 COLLECTION
Cl2, N2
TiO2
SCRUBBER
CALCINER
WATER
TREATMENT AGENT
TREAT
TO WASTE DISPOSAL
FINISHED TiO2
MILLING

FIGURE 8-11-3
STANDARD CHLORIDE PROCESS TITANIUM DIOXIDE FLOW DIAGRAM

by centrifugation or filtration, and the gaseous titanium tetrachloride is condensed. Noncondensable reaction gases containing titanium tetrachloride, silicon tetrachloride and hydrogen chloride are water scrubbed, then vented. A number of techniques are used to further purify the tetrachloride, removing traces of silicon, vanadium, magnesium, manganese, aluminum and chromium. These techniques yield a pure titanium tetrachloride and a wastewater.

After purification, the titanium tetrachloride is vaporized and passed into a reactor with heated air or oxygen. The solid titanium dioxide particles are mechanically separated from the gas stream, calcined, ground, treated and packed.

Wastes contain metal salts, waste coke, hydrochloric acid, titanium hydroxide, dissolved solids.

Sulfate Process V(b) In the sulfate process, titanium dioxide-bearing ores are dissolved in sulfuric acid at high temperatures to produce titanium sulfate as an intermediate product. In some cases, small amounts of antimony trioxide are also added. The acid solution is clarified, a portion of the iron sulfates is removed by crystallization, and the titanium sulfate is hydrolyzed to form a white, non-pigmentary hydrate. The hydrate is calcined to form crystalline titanium dioxide, which is milled, surface treated, and packaged for sale.

Process wastewaters are acidic and contain dissolved and suspended solids and metal salts.

Significant Inorganic Products (1-47)

As shown in the subcategorization section of this report, the significant inorganic products segment of this industry consists of forty seven (47) product subcategories. Processes consist of chemical reactions and/or physical separation techniques from ores or natural brines. The processes and water uses are similar to those described for the major inorganic chemicals, and will not be discussed in detail here.

Wastes contain concentrations of the chemicals in the raw materials, and also concentrations of the products produced. Wastewaters are also generated by auxiliary systems, such as boiler blowdowns, cooling water discharges, equipment cleanups, and spills and leaks.

4. Wastewater Characterization

Table 8-11-1 contains raw wastewater characteristics for the most significant of the subcategories discussed.

5. Control and Treatment Technology

In-Plant Control - The following in-plant controls can reduce wastewater effluent:

a) The use of gas scrubbing and the sale of scrubber wastes, or chemical treatment of scrubber wastes can eliminate the waste stream for Aluminum Chloride (A) and Calcium Oxide and Calcium Hydroxide (E).

b. Recycle of process wastewaters are practiced for Aluminum Sulfate (B) and Sodium Sulfite (S).

c. The substitution of dry bag collector systems for wet scrubber systems have been effective for Calcium Carbide (C) and Calcium Oxide and Calcium Hydroxide (E).

d. Separation of salts in the waste stream, followed by recycle or sale of these salts is utilized for Calcium Chloride (D).

e. The muds produced in Chlorine and Sodium or Potassium Hydroxide (F) can be clarified and disposed of in landfills. The mercury from F(a) can be precipitated with sulfides. Asbestos in the diaphragm cell process F(b) can be filtered or clarified. Some salts can be recycled back into the process.

f. Neutralization followed by precipitation can reduce sulfate and fluoride contents in Hydrofluoric Acid Production (H).

g. Clarification with skimming can reduce the organic solvents and suspended solids in the Hydrogen Peroxide Organic Process I(a). Scrap iron decomposes the Hydrogen Peroxide in the waste stream. The Electrolytic Process I(b), produces a very small process waste stream, and total evaporation has been used to eliminate this stream.

h. Distillation of the brine waste to recover water from the Potassium Sulfate (M) subcategory has been successful in accomplishing a closed cycle plant.

TABLE 8-11-1
INORGANIC CHEMICAL INDUSTRY
RAW WASTEWATER CHARACTERISTICS

	Subcategory									
Parameter (mg/l)	A,B,C,E,G, J,K,L,U	D	F(a)	F(b)	H	I,P,S,R,V	M	N,O	Q	T
Flow (gpd)	No Process Waste	8 MM				No Data	Only Solid Mud Wastes	17 M		
Flow Type		C						C		
BOD (mg/l)		1		0						
TSS		30	5-10	22 M	17 M			200	170 M	2 M
TDS		300		18 M*	4.2M*			76 M	5M-13M*	90 M
COD		-			13					8 M*
pH		7-9	6.7-8.5		4*			11*	10*	11*
Color(APHA Units)		60-80						300		
Alkalinity		235						600		
Mercury			8-45*							
Calcium		170-700			650			45 M		
Fluoride					13					
Chromium(+6)									1300*	
Nitrate									9.8	
Sulfate									3.9 M	
Sulfite										60 M

Notes:
M - 1,000
MM - 1,000,000
B - Batch
C - Continuous
* See Appendix 5 for parameters which may be inhibitory to biological systems.

i. Clarification to settle suspended solids has been practiced by Sodium Bicarbonate (N) and Sodium Carbonate (O) subcategories.

j. Return of the waste waters to the source of the brine materials is usually practiced for Sodium Chloride (P).

k. Separation of the hexavalent chrome stream, chemical reduction to trivalent chrome, followed by precipitation and clarification is practiced for Sodium Dichromate and Sodium Sulfate (Q) production.

l. Clarification of the mud bearing streams with land disposal of the mud is practiced for Sodium Metal (R) production.

m. Conversion of Sulfite to Sulfate followed by recovery of the sulfate can be accomplished for Sodium Sulfite Production (T).

n. Containment of spills and leaks followed by neutralization or recycle is practiced for Sulfuric Acid Production (U). Concentration and recovery of the SO_2 scrubber waste stream can also be practiced.

o. Chemical precipitation followed by clarification and land disposal of sludges is practiced for Titanium Dioxide, Chlorine Process U(a) and Sulfate Process U(b).

Treatment Technology - The type, degree and costs involved depend upon specific circumstances unique for each chemical. Various treatment techniques commonly used in the inorganic chemicals manufacturing industry include settling ponds or vessels, filtration, chemical treatment, centrifugation, evaporation, drying and carbon adsorption.

A number of options for the final disposal of waterborne wastes from inorganic chemical manufacturing are available, depending upon quantity and characteristics of the waste stream. They include discharge to surface water, land disposal, and unlined or lined evaporation ponds.

1. Industry Description

The plastics and synthetics industry is composed of three segments: the manufacture of the raw material or "monomer", the conversion of this monomer into a resin or plastic material, and the conversion of the plastic resin, or polymer, into a plastic item such as a toy, synthetic fiber, packaging film, adhesive, paint, etc.

This description is concerned with the manufacture of the plastic or synthetic resin and the manufacture of synthetic fibers, such as nylon, rayon, cellulose film and others described in the subcategorization section of this industry.

Waste from this industry can be high in BOD, and COD and can contain metals.

This industrial category includes Standard Industrial Classifications (SIC) 2821, 2823, 2824 and 3079.

2. Industrial Categorization

The industry has been categorized according to waste characteristics and subcategorized along product lines as follows:

Main Category I - Generates a low raw waste load (less than 10 units/1000 units of product produced); low BOD concentrations attainable (less than 20 mg/l).

Main Category II - Generates a high waste load (greater than 10 units/1000 units of product); low BOD concentrations attainable (less than 20 mg/l).

Main Category III - Generates a high waste load (greater than 10 units/1000 units of product); medium BOD concentrations attainable (30-75 mg/l).

Main Category IV - Generates a high waste load (greater than 10 units/1000 units of product); high BOD concentrations attainable (over 75 mg/l).

Main Category	Subcategory	Designation
I	Polyvinyl Chloride	A
I	Polyvinyl Acetate	B
I	Polystyrene	C
I	Polypropylene	D
I	Polyethylene	E
II	Cellophane	F
II	Rayon	G
II	ABS/SAN (Acrylonitrile,butadiene, styrene/styrene,acrylonitrile)	H
III	Polyester	I
III	Nylon 66	J
III	Cellulose Acetate	L
IV	Acrylics	M
I	Ethylene-Vinyl Acetate	N
I	Polytetrafluoroethylene	O
I	Polypropylene Fibers	P
III	Alkyds/Polyester Resins	Q
III	Cellulose Nitrate	R
III	Polyamides	S
III	Polyesters (thermoplastic)	T
III	Silicones	U
III	Epoxy Resin	V
IV	Phenolic Resin	W
IV	Urea & Melamine	X

3. Process Description

Polymerization is the formation of long chain molecules from a single type molecule, or "monomer". For example:

Monomer A + monomer A → -A-A-A-A-A-(polymer)

Copolymers are formed by combining two different monomers. For example:

Monomer A + monomer B → -A-B-A-B-A-(copolymer)

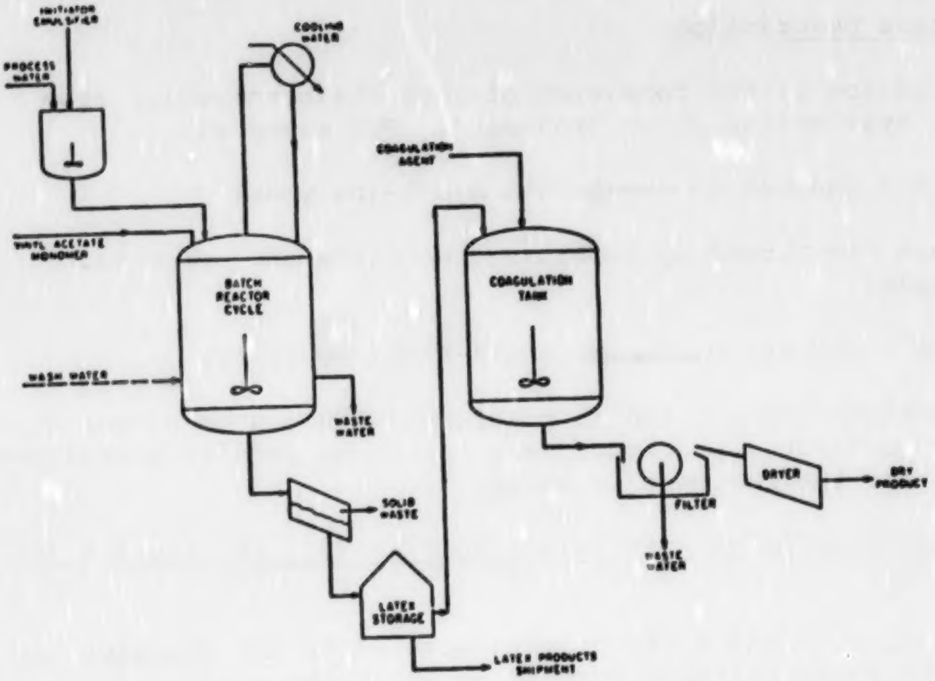
Polymerization takes place in reactors which can be either a batch or continuous process. Many reactions require a catalyst in order for the reaction to occur.

Polyvinyl Chloride (A), Polyvinyl Acetate (B), Polystyrene (C) ABS/SAN (H)

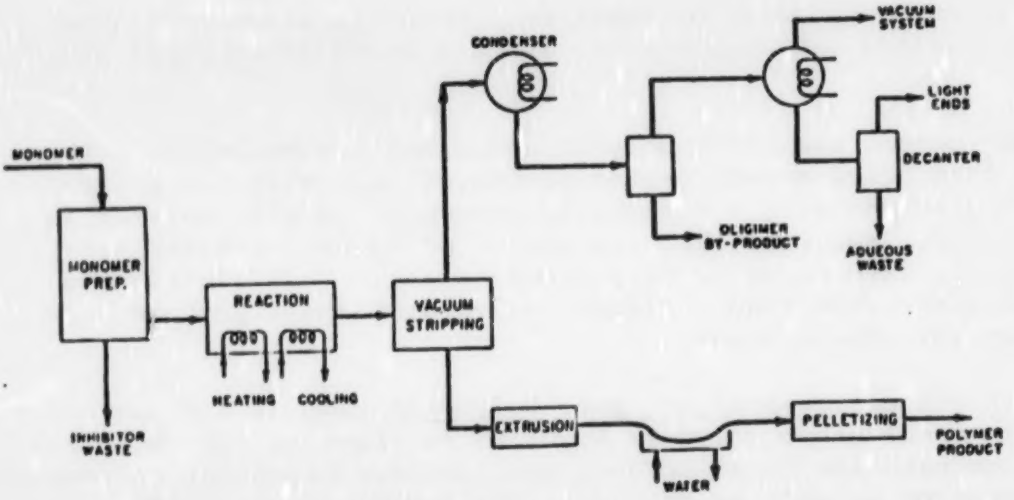
Polymers A, B, C and H can be manufactured by the Emulsion and Suspension Polymerization process in which the monomer is dispersed in an aqueous, continuous phase during the course of the reaction. The batch cycle consists of the continuous introduction of a water-monomer emulsion to a stirred, temperature controlled reactor ranging in size from 5,000-30,000 gallons. On completion of a batch, a short "soaking" time is allowed for completion of reaction. Water is added to dilute to the desired end composition, and the batch is screened and stored.

In some cases, the water-polymer emulsions are marketed in this latex form, thus no wastewater is generated. When the polymer is isolated and sold a wastewater contaminated with polymer is discharged. Monomers that are protected by an inhibitor are subject to washing prior to polymerization. This contributes to the wastewater load. Figure 8-12-1 contains a process flow diagram for this process.

Atmospheric or Low-Pressure Mass Polymerization is a process used to manufacture polymers A, C, H, as shown on Figure 8-12-1. Reaction rate and final product obtained are dependent on temperature control as well as catalysts and modifiers used. The catalyst and modifier remain in the product. Inhibitors are usually added to the monomer for protection during storage. This is removed by washing, thus generating a wastewater. During separation of the unreacted monomer and contaminants from the product by vacuum stripping, a waste stream containing these chemicals is produced.


INITIATOR EMULSIFIER
PROCESS WATER
COOLING WATER
VINYL ACETATE MONOMER
BATCH REACTOR CYCLE
WASH WATER
WASTE WATER
SOLID WASTE
LATEX STORAGE
LATEX PRODUCTS SHIPMENT
COAGULATION AGENT
COAGULATION TANK
FILTER
WASTE WATER
DRYER
DRY PRODUCT

EMULSION POLYMERIZATION (A, B, C, H)


MONOMER
MONOMER PREP.
INHIBITOR WASTE
REACTION
HEATING
COOLING
VACUUM STRIPPING
CONDENSER
OLIGIMER BY-PRODUCT
VACUUM SYSTEM
LIGHT ENDS
DECANTER
AQUEOUS WASTE
EXTRUSION
WATER
PELLETIZING
POLYMER PRODUCT

MASS POLYMERIZATION (A, C, H)

FIGURE 8-12-1
POLYMERIZATION

Polyethylene (E)

Ethylene gas is mixed with a very small quantity of catalyst and raised to a high pressure in the High Pressure Mass Polymerization process. At the appropriate pressure and temperature, polymerization is carried out in jacketed (cooled) tubular reactors. On completion of the reaction, the polymer is flash cooled in drums containing water. The low density polyethylene is then formed into pellets and separated from the water. The water is recycled, but is periodically purged producing a waste stream.

Polyethylene (E) and copolymers can be manufactured by the Solution Polymerization process, in which the polymer is dissolved in the reaction solvent as it is formed, and the catalyst is present as a separate solid phase. The catalyst system is activated chromium oxide deposited on a carrier such as alumina. After reaction the catalyst and solvent are separated from the polymer and then separated from each other.

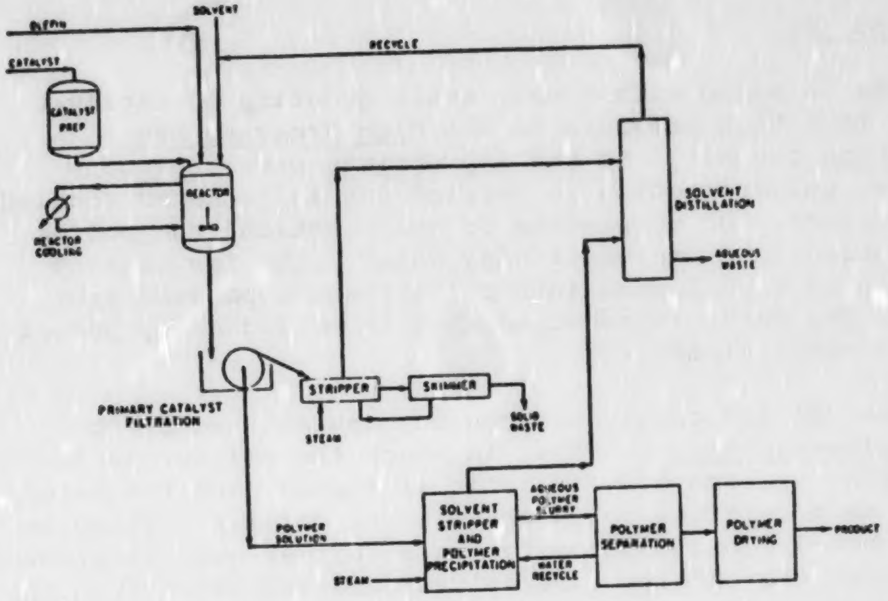
The water used in the separation processes constitutes a waste stream, which will contain quantities of catalyst, solvent and polymer. A process flow diagram is shown in Figure 8-12-2.

Polyethylene (E), Polypropylene (D), and some copolymers can be manufactured by the Ziegler Process. This process is similar to the Solution Polymerization Process except that the polymer precipitates as it is formed rather than remaining in solution. Products of this process include: high density-polyethylene, Polypropylene, polybutene, copolymers. Wastewaters contain solvent (aqueous alcohols).

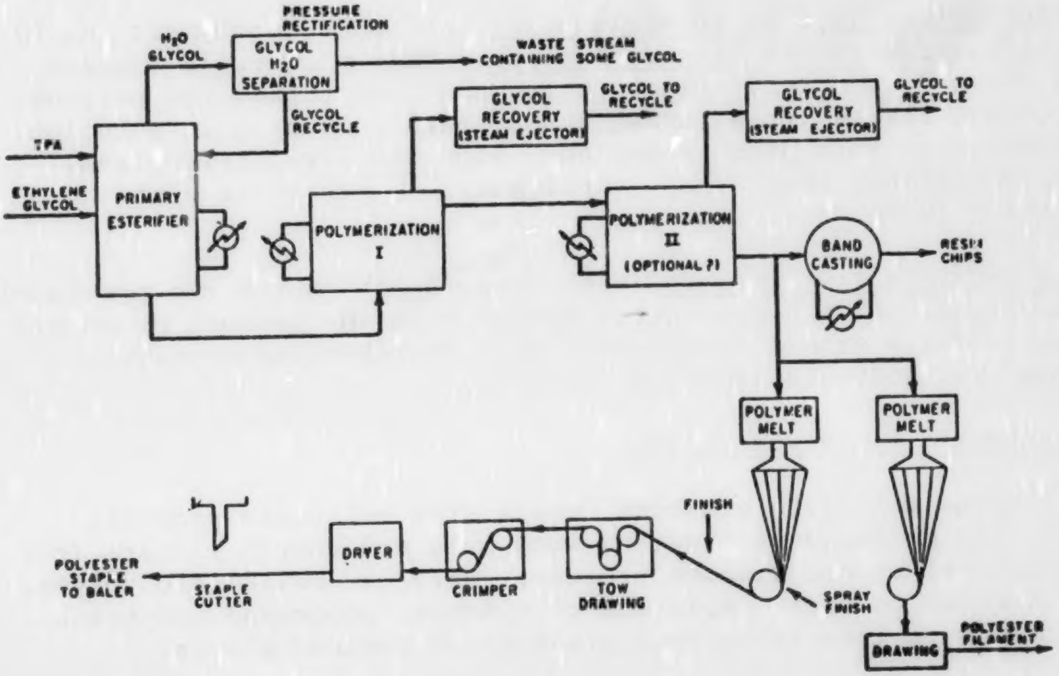
The Particle Form Process is an improvement on the two previously described, using a continuous system with the product drawn off continuously from a "loop" reactor. Wastes contain polymer fines and solvents (aqueous alcohols).

Cellophane and Rayon (F)(G)

Cellophane and Rayon are both regenerated cellulose products that are produced by treating wood pulp and cotton linters (raw cellulose) by the Viscose process. Here raw cellulosic polymer is treated to form a solution of viscose, processed and transformed back into cellulosic plastics of desired shapes.


OLEFIN
SOLVENT
CATALYST
CATALYST PREP
RECYCLE
REACTOR
REACTOR COOLING
SOLVENT DISTILLATION
AQUEOUS WASTE
STRIPPER
SKIMMER
PRIMARY CATALYST FILTRATION
STEAM
SOLID WASTE
SOLVENT STRIPPER AND POLYMER PRECIPITATION
AQUEOUS POLYMER SLURRY
POLYMER SEPARATION
POLYMER DRYING
PRODUCT
POLYMER SOLUTION
STEAM
WATER RECYCLE

POLYOLEFIN PRODUCTION - SOLUTION PROCESS (E)


PRESSURE RECTIFICATION
H_2O GLYCOL
GLYCOL H_2O SEPARATION
WASTE STREAM CONTAINING SOME GLYCOL
GLYCOL RECYCLE
GLYCOL RECOVERY (STEAM EJECTOR)
GLYCOL TO RECYCLE
GLYCOL RECOVERY (STEAM EJECTOR)
GLYCOL TO RECYCLE
TPA
ETHYLENE GLYCOL
PRIMARY ESTERIFIER
POLYMERIZATION I
POLYMERIZATION II (OPTIONAL ?)
BAND CASTING
RESIN CHIPS
POLYMER MELT
POLYMER MELT
FINISH
POLYESTER STAPLE TO BALER
STAPLE CUTTER
DRYER
CRIMPER
TOW DRAWING
SPRAY FINISH
DRAWING
POLYESTER FILAMENT

POLYESTER FIBER AND RESIN PRODUCTION(I)

FIGURE 8-12-2
POLYMERIZATION
PLASTIC AND SYNTHETICS

Cellophane manufacture is performed in three steps: (1) Viscose preparation, (2) Film casting and (3) Film Coating. Viscose is prepared in several batch operations in which the raw cellulose is depolymerized in a caustic solution and is then reacted with carbon disulfide to make a solution of sodium cellulose xanthate called viscose. This solution is reacted with sulfuric acid in the next step to regenerate the cellulose as cellophane. The caustic solution in the first step is recycled but is periodically purged, producing a waste stream.

Film is cast by pumping "viscose" through slit-dies into a spinning bath of sulfuric acid and sodium sulfate. The cellophane film is subsequently passed through finishing baths, is dried and is wound into rolls. In the third step, coatings are applied to the film from organic solvent solutions. The solvent from these solutions is recovered and reused.

Waste liquors from the spinning bath are evaporated, crystallized, and recycled.

Rayon (G) is manufactured by the same process as cellophane except the regenerated cellulose is recovered as fibers instead of as film.

Purging of recycled solutions constitute a waste stream.

ABS/SAN (H)

Included in Description (A).

Polyester Resin and Fiber (I)

In this process, the monomer is generated first, then followed by polymerization. Although many plants still use the batch polymerization process, continuous polymerization with direct spinning of the fiber are more common for new facilities. A process flow diagram is shown in Figure 8-12-2. The ester monomer is made by reacting an alcohol, usually ethylene glycol with an ester forming an "activated" ester.

When the polymerization of the ester takes place continuously, the molten polymer is fed to spinning heads, forming the polyester fiber. Wastes associated with this process are primarily unused monomer and methanol.

Nylon 66 Resin and Fibers (J)

This process is similar to polyester in that the monomer is generated first, followed by polymerization. Effluents from activated carbon filtration, evaporators, and scrubbers all produce waste streams containing small amounts of raw and intermediate chemicals.

Nylon 6 Resin and Fibers (K)

Caprolactam is mixed with catalyst, acetic acid and titanium dioxide and polymerized. Formation of the resin into strands and chips as well as monomer recovery processes involve extensive water use.

Cellulose Acetate Resin and Fibers (L)

Cellulose Acetate resin is produced by a batch operation in which wood pulp is dissolved with strongly acidic materials and cellulose acetate "flakes" are recovered by an acid reaction to form a precipitate. The polymer "flakes" are washed to recover the acids used in the process. Wastewaters are high in dissolved solids.

The fibers are manufactured by dissolving in acetone the "flakes" produced by the previous process and by pumping the "dope" solution through spinnerettes. The acetone solvent recovery system is the major source of waste.

Acrylics (M)

Acrylonitrile monomer is polymerized in a continuous reactor in the presence of a catalyst. The polymer is recovered, dried, and forced through spinnerettes. Solvent losses are a major contributor to the waste load.

Ethylene-Vinyl Acetate Copolymers (N)

Ethylene-Vinyl Acetate (EVA) is manufactured in the same facilities as low and high density polyethylene (E). The monomers used in the reaction are vinyl acetate and ethylene. Polymerization is carried out in an autoclave. The reaction mass is then sent to a separator, to remove unreacted monomers. The EVA polymer is then fed to an extruder which forms strands, which are then cut into pellets.

The cooling water used in the pelletizer is recirculated, but is purged periodically, producing a waste stream containing monomers and polymer fines.

Polytetrafluoroethylene (PTFE) (O)

The TFE monomer is produced in the gaseous phase. The product stream is scrubbed with water and then with dilute caustic solution to remove byproduct acid and other soluble components. The gas is then dried with concentrated sulfuric acid or ethylene glycol.

The waste stream produced from the scrubbing processes is acidic and contains fluoride. If glycol is used as the drying agent, it contributes to the waste load. PTFE polymer is produced in a batch operation and sold in a granular or pellet form, fine powder, or in an aqueous dispersion.

Polypropylene Fibers (P)

The polymerization process has been described under subcategory D, the Ziegler Process. Polypropylene fibers are made by melt spinning. The process consists of coloring polypropylene flakes by dry blending the flakes with pigments, followed by a melting and extrusion process that forms colored polypropylene pellets. The pellets are then extruded through a spinnerette into a column of air which solidifies the molten filaments. The filaments are then stretched or spun into fibers.

Rinsewaters are generated from the blending process. Discharges from spinning wastes are very high in BOD.

Alkyds and Unsaturated Polyester Resins (Q)

Unsaturated polyester resins are made in a batch process by an esterification reaction involving several materials derived from petroleum fractions. Reinforced plastic is made by reinforcing the resin with glass or metallic fibers. Nonreinforced unsaturated polyester resin is used for castings, coatings and putty-like compounds.

Alkyds are often manufactured and used interchangeably with unsaturated polyesters, since they are chemically very similar. They are used for paint formulations and in molding compounds.

Wastewaters contain a variety of contaminants as a result of the polymerization reaction, scrubbers, and equipment washouts, which are high in BOD, COD, grease and oil.

Cellulose Nitrate (R)

Cellulose Nitrate is produced by reacting cellulose with a mixture of nitric and sulfuric acids followed by:

Washing to remove acid

Stabilization by boiling with water

Digestion (heating in water)

Dehydration

Wastewaters contain acids, unrecovered alcohols, and suspended solids.

Polyamides - (Nylon 6/12) (S)

Nylon 6/12 is produced in equipment used regularly for the production of Nylon 66 and the wastes are similar.

Polyester Resins (thermoplastic) (T)

These resins are produced by the same polymerization process used for fiber production (I). The two raw materials are ethylene glycol and either dimethyl terephthalate (DMT) or terephthalic acid (TPA). The two reactants are polymerized in a reactor. Some integrated plants also produce polyester fibers.

Liquid wastes result from the condensation of steam ejector vapors. Process materials are present in the waste streams.

Silicones (U)

Plants purchase silicon metal and react it with a wide range of chemicals to produce silicone. In general, silicones are produced by reacting chloride containing compounds, such as methyl chloride or phenyl chloride with silicon metal in the presence of copper catalyst to form chlorosilane, which is a silicone.

A significant amount of acid wastes often containing copper are generated due to the formation of hydrochloric acid (HCl) in the process. In addition, trace amounts of solvent may be present in the waste stream.

Epoxy Resins (V)

The epoxy resin family should be regarded as intermediates rather than an end resin itself since they require further reaction with a second component, or curing agent in order to yield the final thermoset material. Almost all commercially produced epoxy resins are made by the reaction between epichlorohydrin and bisphenol A. The reaction takes place under alkaline conditions.

The epoxy resins fall into two broad categories: the low molecular weight liquids and the high molecular weight solids. The low molecular weight liquid resins can be manufactured by either batch or continuous processes, while solid resins are produced by batch processes. Wastewaters contain caustic and salt.

Phenolic Resins (W)

These resins are based upon the reaction between phenol and formaldehyde. There are two broad types of resins produced by the industry: resols and novolaks. Resols are formed from a mixture containing an excess of formaldehyde; novolaks are formed from a mixture containing a deficiency of formaldehyde. These resins are generally produced by a batch process.

Wastewaters are generated from the distillation process and the rinsing procedures.

Urea and Melamine (X) (Amino Resins)

"Amino Resins" are a broad group of polymers formed by batch process from formaldehyde and various nitrogen containing organic chemicals such as urea and melamine. The product can be sold either as a thick syrup or as a solid.

The equipment used for the production of the "first-step" amino resins is often also used for the production of other resins such as phenolics. Between these different uses, and between production batches of melamine and urea resins, it is customary to clean the equipment with hot dilute caustic solution. This material is drained as process waste.

4. Wastewater Characterization

Tables 8-12-1 and 8-12-2 contain raw wastewater characteristics for the industry.

TABLE 8-12-1
PLASTICS AND SYNTHETICS INDUSTRY
RAW WASTEWATER CHARACTERISTICS

WASTE PARAMETER (mg/l)	SUBCATEGORIES A	B	C	D	E+	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X
Flow GPD	0.6MM	0.3MM			0.8MM		8.3MM	1.4MM	0.8MM	0.41MM	1.0MM		2.74MM	10MM			530-45M				270M-7MM			
Flow Type	B	B	B	B	B			B	B-C			B					B					B-C	B	B
BOD	350	1500 *			400		200	1200 *	4400*	1300*	400		900*	160			3000*				300	850*	1500*	1300 *
TSS																								
COD	1600*	-			1500*		500	2100 *	5800*	2100*	-		1700*				4000*				700	2300*	5000*	6500 *
COLOR	)																							
MERCURY	)																							
CHROMIUM	)																							
COPPER	)																							
ZINC	)																							
CYANIDES	)May be Present in all Subcategories																							
COBALT	)																							
IRON	)																							
TITANIUM	)																							
CADMIUM	)																							
NICKEL	)																							
VANADIUM	)																							
OIL AND GREASE	)																							

B - Bath Process
C - Continuous Process
NOTE - M - = 1,000
MM = 1,000,000
+ Low Density Polyethylene
* See Appendix 5 for parameters which may be inhibitory to biological systems.

TABLE 8-12-2
WASTEWATER CHARACTERIZATION
PLASTICS AND SYNTHETICS INDUSTRY
PRODUCTION BASED DATA
SUBCATEGORIES

WASTE PARAMETER	A	B	C	D	E	F	G	H	I	J	K	L
Flow Range - CM/KKG (1)	2.5 - 42	0 - 25	0 - 142	2.5 - 67	0-42	100 - 560	33 - 192	1.7 - 24	0 - 170	0-152	0-152	16 - 420
Flow Type												
BOD Kg/KKG (2)	0.1 - 48	0 - 2	0 - 3	0 - 10	0-5	20 - 133	20 - 45	2 - 21	3 - 20	0-135	0-135	6 - 70
TTS Kg/KKG	1 - 30	0 - 2	0 - 8.4	-	0-4	6 - 70	-	0 - 30	0 - 12	0-8	0-8	2 - 20
COD Kg/KKG	0.2 - 100	0 - 3	0 - 6	0 - 20	0-54	40 - 334	33 - 100	5 - 34	6 - 45	0-300	0-300	11 - 100
Zinc							12 - 50					

WASTE PARAMETER	M	N	O	P	Q	R	S	T	U	V	W	X
Flow Range - CM/KKG (1)	2.5 - 51	2.3 - 2.5	18 - 153	1 - 3 - 31	0.3 - 12	111 - 170	-	2.2 - 6.4	8.3 - 280	2.5 - 5	0.5 - 20	≃ 1
Flow Type												
BOD Kg/KKG (2)	10 - 40	0.4 - 4.4	0 - 7	0.4 - 1	9 - 25	55 - 110	-	0 - 10	5 - 110	60 - 85	15 - 50	≃ 13
TTS Kg KKG	0 - 2	0 - 4	2.2 - 6.6	0.2 - 2.2	1 - 2	35	-	-	≃ 50	5 - 25	0 - 7	-
COD KG/KKG	10 - 70	0.2 - 54*	4.4 - 44	1.8 - 3	15 - 80	75 - 275	-	1 - 30	15 - 300	30 - 127	90 - 65	≃ 60

(1) CM/KKG Cubic Meters/1000 kg product produced/
(2) KG/KKG (kilograms/1000 kg product produced)

5. Control and Treatment Technology

In-Plant Control

A major source of waterborne pollutants is attributable to spills, leaks and accidents. The following list of spill prevention and control techniques apply to the synthetic and plastic industry:

Dike areas around storage tanks

Install tank level indicators and alarms

Curb process areas

Install holding lagoons for general plant area

Treatment Technology

Wastewater treatment technology in this industry relies heavily upon the use of biological treatment methods preceded by pH adjustment, equalization, and primary solids removal.

COD/BOD ratios in the plastics and synthetic industry range from 4-12, which indicate the presence of substances which are not biodegradable. Removal efficiencies of these substances vary markedly from one subcategory to another. In general, longer residence times are required to treat wastes from this industry than for municipal wastes. Detention times of 500-900 hours have been reported for some plants. Of all the subcategories, acrylic wastes represent the most difficult treatment problems. Equalization prior to discharge to municipal treatment plant can help to maximize POTW efficiency.

Water recycle has not been practiced due to two factors: (1) The industry, except for cellulosics, is a relatively low user of water per unit of product, and (2) High quality process water is often required in order to maintain product quality.

Table 8-12-3 gives removal efficiencies for certain treatment methods practiced by this industry.

TABLE 8-12-3

Plastics and Synthetics Industry

Wastewater Treatment Practices

	Removal Efficiencies (%)	
BOD Removal	Subcategories G, K,M, R, U	Subcategories A,B,E,H,I,J,Q,V,X
Neutralization, Equalization, Clarification, and Biological Treatment	80-87	95-99
COD Removal	Subcategories B, G	Subcategories D,M, U
Neutralization, Equalization, Clarification, and Biological Treatment	0-30	60-70
	Subcategories V, W	Subcategories A,E,H,I,J,N,Q,X
	85	90-95

1. Industry Description

The Soap and Detergent Industry produces liquid and solid cleaning agents for domestic and industrial use, including laundry, dishwashing, bar soaps, specialty cleaners and industrial cleaning products. The discharges are generally non-toxic and readily responsive to treatment except in the industrial surfactant area. More than 95% of plant effluents go to municipal treatment plants.

The industry is broadly divided into two categories: soap manufacture which is based on processing of natural fat, and detergent manufacture which is based on the processing of petrochemicals.

This industrial category includes Standard Industrial Classification (SIC) 2841 and includes establishments primarily engaged in manufacture of soap, synthetic organic detergents, inorganic alkaline detergents or any combinations thereof and establishments producing crude and refined glycerine from vegetable and animal fats and oils. Excluded from this category are establishments primarily engaged in the manufacturing of shampoo or shaving products whether from soap or synthetic detergents (SIC 2844) and the synthetic glycerine industry (SIC 2869). Also excluded are specialty cleaners, polishing and sanitation preparations.

2. Industrial Categorization

A useful categorization system for the purposes of raw waste characterization and the establishment of pretreatment information are the following subcategories:

SOAP AND DETERGENT CATEGORIZATION

Main Category	Subcategory	Designation
Soap Manufacture	Batch Kettle and Continuous	A
	Fatty Acid Manufacture by Fat Splitting	B
	Soap from Fatty Acid Neutralization	C
	Glycerine Recovery	
	Glycerine Concentration	D
	Glycerine Distillation	E
	Soap Flakes and Powders	F
	Bar Soaps	G
	Liquid Soap	H
Detergent Manufacture	Oleum Sulfonation & Sulfation (Batch & Continuous)	I
	Air-SO_3 Sulfation & Sulfonation (Batch & Continuous)	J
	SO_3 Solvent & Vacuum Sulfonation	K

Soap and Detergent Categorization continued

Main Category	Subcategory	Designation
	Sulfamic Acid Sulfation	L
	Chlorosulfonic Acid Sulfation	M
	Neutralization of Sulfuric Acid Esters & Sulfonic Acids	N
	Spray Dried Detergents	O
	Liquid Detergent Manufacture	P
	Detergent Manufacturing by Dry Blending	Q
	Drum Dried Detergents	R
	Detergent Bars & Cakes	S

3. Process Description

A flow diagram for the entire industry is shown in Figure 8-13-1.

Soap Manufacture and Processing

Soap manufacturing consists of two major operations: the production of neat soap (65-70% hot soap solution) and the preparation and packaging of finished products into flakes and powders, (F), bar soaps (G) and liquid soaps (H). Many producers of neat soap also recover glycerine as a by-product for subsequent concentration (D) and distillation (E).

Neat soap is generally produced in either of two processes:

a. The batch kettle process (A), or

b. The fatty acid neutralization process, which is preceded by the fat splitting process (B,C).

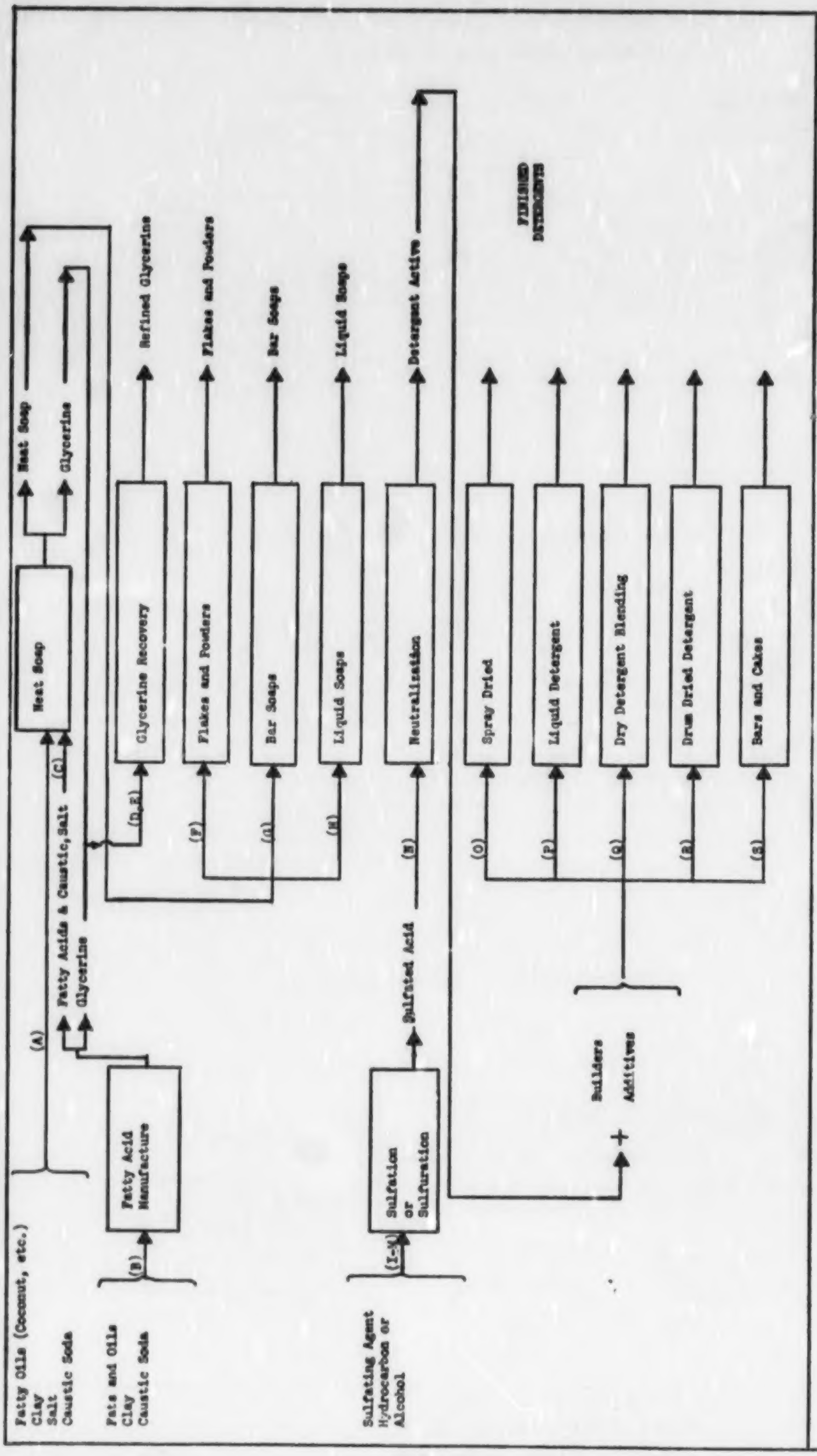
Descriptions of the production of neat soap will follow. Process flow diagrams are shown in Figure 8-13-2.

Production of Neat Soap

Batch Kettle Process (A) - The production of neat soap by batch kettle consists of the following operations:

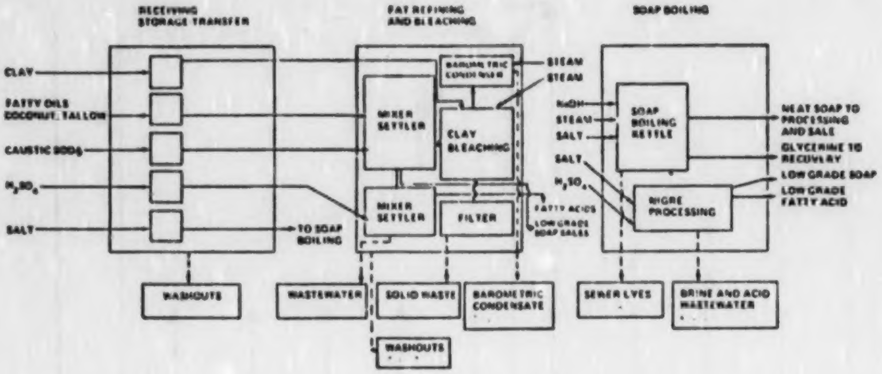
- Receiving and Storage of Raw Materials
- Fat Refining and Bleaching
- Soap Boiling

The major wastewater sources are the washouts of both the storage and the refining tanks, as well as from leaks and spills of fats and oils around these tanks. These streams are usually skimmed for fat recovery prior to discharge to the sewer.

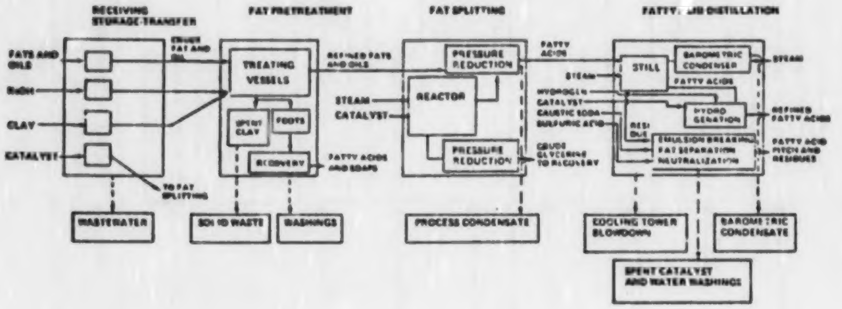

Fatty Oils (Coconut, etc.)
Clay
Salt
Caustic Soda
(A)
Neat Soap
Neat Soap
Glycerine
Fats and Oils
Clay
Caustic Soda
(B)
Fatty Acid Manufacture
Fatty Acids & Caustic, Salt
Glycerine
(C)
(D,E)
Glycerine Recovery
Refined Glycerine
(F)
Flakes and Powders
Flakes and Powders
(G)
Bar Soaps
Bar Soaps
(H)
Liquid Soaps
Liquid Soaps
Sulfating Agent
Hydrocarbon or
Alcohol
(I-M)
Sulfation
or
Sulfuration
Sulfated Acid
(N)
Neutralization
Detergent Active
FINISHED
DETERGENTS
Builders
Additives
+
(O)
Spray Dried
(P)
Liquid Detergent
(Q)
Dry Detergent Blending
(R)
Drum Dried Detergent
(S)
Bars and Cakes

SOAP AND DETERGENT MANUFACTURE
Figure 8-13-1

SOAP MANUFACTURE BY BATCH KETTLE (A)


RECEIVING
STORAGE TRANSFER
FAT REFINING
AND BLEACHING
SOAP BOILING
CLAY
FATTY OILS
COCONUT, TALLOW
CAUSTIC SODA
H_2SO_4
SALT
TO SOAP
BOILING
BAROMETRIC
CONDENSER
STEAM
STEAM
MIXER
SETTLER
CLAY
BLEACHING
MIXER
SETTLER
FILTER
FATTY ACIDS
LOW GRADE
SOAP SALES
NaOH
STEAM
SALT
SOAP
BOILING
KETTLE
SALT
H_2SO_4
NIGRE
PROCESSING
NEAT SOAP TO
PROCESSING
AND SALE
GLYCERINE TO
RECOVERY
LOW GRADE SOAP
LOW GRADE
FATTY ACID
WASHOUTS
WASTEWATER
SOLID WASTE
BAROMETRIC
CONDENSATE
SEWER LYES
BRINE AND ACID
WASTEWATER
WASHOUTS

FATTY ACID MANUFACTURE BY FAT SPLITTING (B)


RECEIVING
STORAGE-TRANSFER
FAT PRETREATMENT
FAT SPLITTING
FATTY ACID DISTILLATION
FATS AND
OILS
NaOH
CLAY
CATALYST
CRUDE
FAT AND
OIL
TO FAT
SPLITTING
TREATING
VESSELS
SPENT
CLAY
FOOTS
RECOVERY
REFINED FATS
AND OILS
FATTY ACIDS
AND SOAPS
PRESSURE
REDUCTION
STEAM
CATALYST
REACTOR
PRESSURE
REDUCTION
FATTY
ACIDS
CRUDE
GLYCERINE
TO RECOVERY
STILL
BAROMETRIC
CONDENSER
STEAM
STEAM
FATTY ACIDS
HYDROGEN
CATALYST
CAUSTIC SODA
SULFURIC ACID
HYDRO
GENATION
RESI
DUE
EMULSION BREAKING
FAT SEPARATION
NEUTRALIZATION
REFINED
FATTY ACIDS
FATTY ACID
PITCH AND
RESIDUES
WASTEWATER
SOLID WASTE
WASHINGS
PROCESS CONDENSATE
COOLING TOWER
BLOWDOWN
BAROMETRIC
CONDENSATE
SPENT CATALYST
AND WATER WASHINGS

SOAP FROM FATTY ACID NEUTRALIZATION (C)

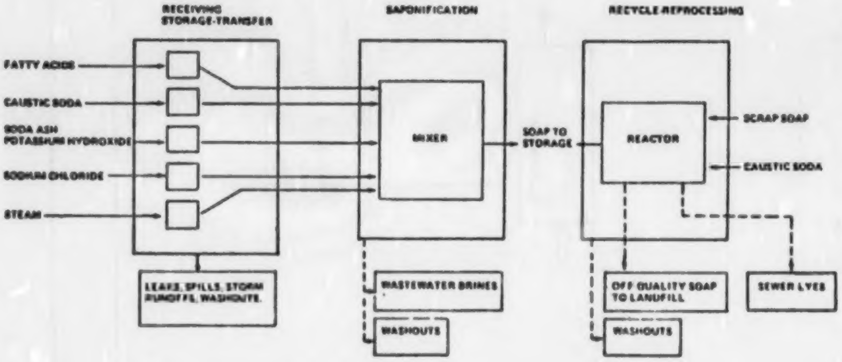

RECEIVING
STORAGE-TRANSFER
SAPONIFICATION
RECYCLE-REPROCESSING
FATTY ACIDS
CAUSTIC SODA
SODA ASH
POTASSIUM HYDROXIDE
SODIUM CHLORIDE
STEAM
MIXER
SOAP TO
STORAGE
REACTOR
SCRAP SOAP
CAUSTIC SODA
LEAKS, SPILLS, STORM
RUNOFFS, WASHOUTS.
WASTEWATER BRINES
WASHOUTS
OFF QUALITY SOAP
TO LANDFILL
SEWER LYES
WASHOUTS

FIGURE 8-13-2
NEAT SOAP MANUFACTURE
PROCESS FLOW DIAGRAMS

The fat refining and bleaching operation is carried out to remove impurities which would cause color and odor in the finished soap. The wastewater from this source has a high soap concentration, treatment chemicals, fatty impurities, emulsified fats, and sulfuric acid solutions of fatty acids. Where steam is used for heating, the condensate may contain low molecular weight fatty acids, which are highly odorous, partially soluble materials.

The soap boiling process produces two concentrated waste streams: sewer lyes which result from the reclaiming of scrap soap and the brine from Nigre processing. Both of these wastes are low volume, high pH with BOD's as high as 45,000 mg/l.

Fatty Acid Neutralization (C) - Soap produced by the neutralization process is a two step process:

Fat + Water---- Fatty Acid + Glycerine (Fat Splitting) (B)

Fatty Acid + Caustic ---- Soap (Fatty Acid Neutralization) (C)

Fat Splitting - The manufacture of fatty acid from fat is called fat splitting (B). Washouts from the storage, transfer and pretreatment stages are the same as those for process (A). Process condensate and barometric condensate from fat splitting will be contaminated with fatty acids and glycerine streams, which are settled and skimmed to recover the insoluble fatty acids which are processed for sale. The water will typically circulate through a cooling tower and be reused. Occasional purges of part of this stream to the sewer releases high concentrations of BOD and some grease and oil.

In the fatty acid distillation process, wastewater is generated as a result of an acidification process, which breaks the emulsion. This wastewater is neutralized and sent to the sewer. It will contain salt from the neutralization, zinc and alkaline earth metal salts from the fat splitting catalyst and emulsified fatty acids and fatty acid polymers.

Fatty Acid Neutralization (C) - Soapmaking by fatty acid neutralization is a faster process than the kettle boil process and generates less wastewater effluent. Becuase it is faster, simpler and cleaner than the kettle boil process, it is the preferred process among the larger as well as the smaller manufacturers.

Often, sodium carbonate is used in place of caustic. When liquid soaps (at room temperature) are desired, the more soluble potassium soaps are made by substituting potassium hydroxide for the sodium hydroxide (lye). This process is relatively simple and high purity raw materials are converted to soap with essentially no by-products. Leaks, spills, storm runoff and washouts are absent. There is only one wastewater of consequence - the sewer lyes from reclaiming of scrap. The sewer lyes contain the excess caustic soda and salt added to grain out the soap. Also, they contain some dirt and paper not removed in the strainer.

Glycerine Recovery Process (D,E)- A process flow diagram for the glycerine recovery process uses the glycerine by-products from kettle boiling (A) and fat splitting (B). The process consists of three steps:

1. Pretreatment to remove impurities
2. Concentration of glycerine by evaporation
3. Distillation to a finished product of 98% purity (See Figure 8-13-3)

There are three wastewaters of consequence from this process: Two barometric condensates - one from evaporation; one from distillation; plus the glycerine foots or still bottoms. Contaminants from the condensates are essentially glycerine with a little entrained salt. In the distillation process, the glycerine foots or still bottoms leave a glassy dark brown amorphous solid rich in salt which is disposed of into the wastewater stream. It contains glycerine, glycerine polymers and salt. The organics will contribute to BOD_5, COD and dissolved solids. The sodium chloride will also contribute to dissolved solids. Little or no suspended solids, oil and grease or pH effect should be seen.

Glycerine can also be purified by use of ion exchange resins to remove the sodium chloride salt followed by evaporation of the water. This process puts additional salts into the wastewater but results in less organic contamination.

Production of Finished Soaps

The production of finished soaps utilizes the neat soap produced in processes A and C to prepare and package finished soap. These finished products are soap flakes and powders(F), bar soaps (G) and liquid soap (H). See Figure 8-13-4.

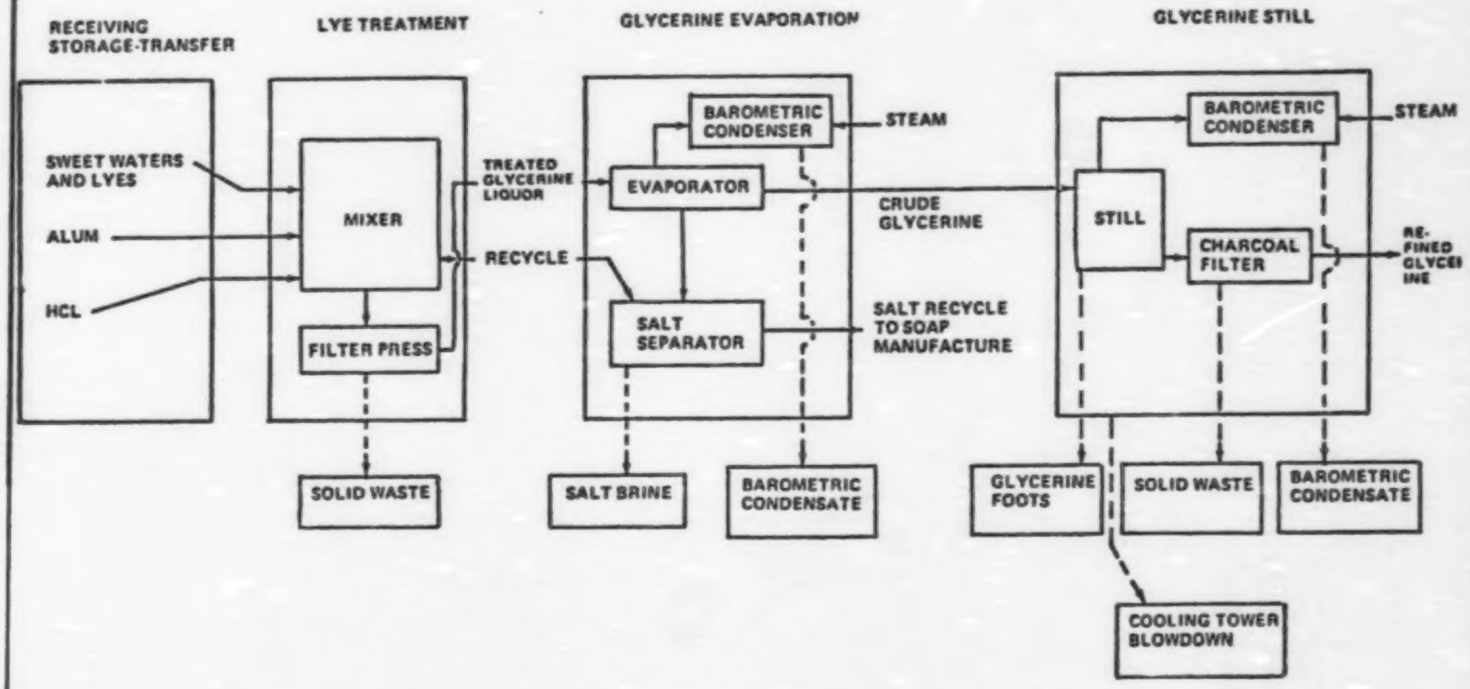
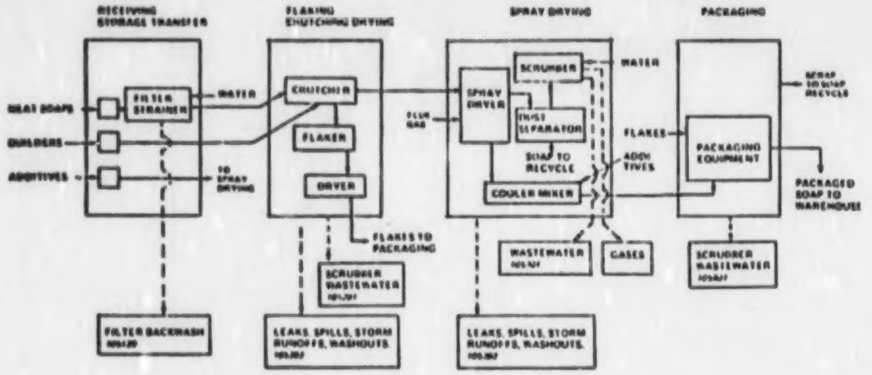

RECEIVING STORAGE-TRANSFER
LYE TREATMENT
GLYCERINE EVAPORATION
GLYCERINE STILL
SWEET WATERS AND LYES
ALUM
HCL
MIXER
FILTER PRESS
SOLID WASTE
TREATED GLYCERINE LIQUOR
RECYCLE
EVAPORATOR
BAROMETRIC CONDENSER
STEAM
SALT SEPARATOR
SALT BRINE
BAROMETRIC CONDENSATE
CRUDE GLYCERINE
SALT RECYCLE TO SOAP MANUFACTURE
STILL
BAROMETRIC CONDENSER
STEAM
CHARCOAL FILTER
RE-FINED GLYCERINE
GLYCERINE FOOTS
SOLID WASTE
BAROMETRIC CONDENSATE
COOLING TOWER BLOWDOWN

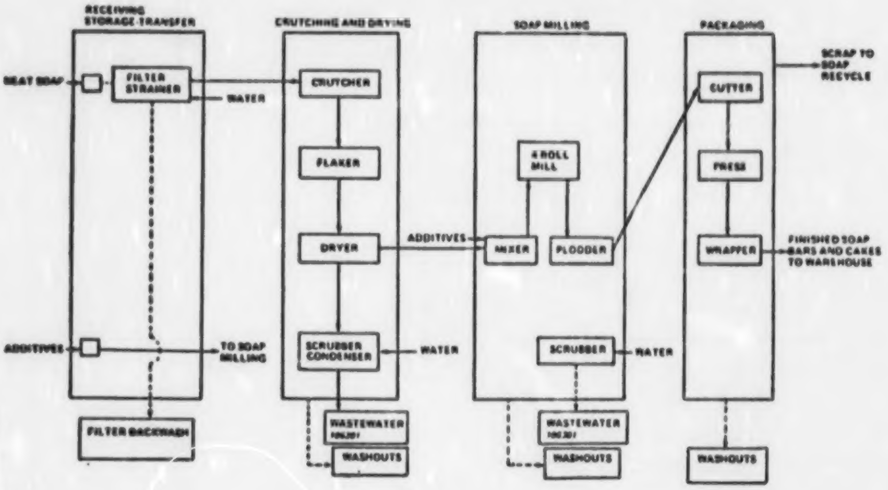
FIGURE 8-13-3 (D,E)

GLYCERINE RECOVERY
PROCESS FLOW DIAGRAM

SOAP FLAKES AND POWDERS (F)


RECEIVING STORAGE TRANSFER
FLAKING CRUTCHING DRYING
SPRAY DRYING
PACKAGING
NEAT SOAPS
BUILDERS
ADDITIVES
FILTER STRAINER
WATER
TO SPRAY DRYING
CRUTCHER
FLAKER
DRYER
FLAKES TO PACKAGING
SCRUBBER WASTEWATER
FILTER BACKWASH
LEAKS, SPILLS, STORM RUNOFFS, WASHOUTS
FLUE GAS
SPRAY DRYER
SCRUBBER
WATER
MIST SEPARATOR
SOAP TO RECYCLE
ADDI TIVES
COOLER MIXER
WASTEWATER
GASES
LEAKS, SPILLS, STORM RUNOFFS, WASHOUTS
FLAKES
PACKAGING EQUIPMENT
SCRAP TO SOAP RECYCLE
PACKAGED SOAP TO WAREHOUSE
SCRUBBER WASTEWATER

BAR SOAPS (G)


RECEIVING STORAGE TRANSFER
CRUTCHING AND DRYING
SOAP MILLING
PACKAGING
NEAT SOAP
FILTER STRAINER
WATER
CRUTCHER
FLAKER
DRYER
ADDITIVES
TO SOAP MILLING
FILTER BACKWASH
SCRUBBER CONDENSER
WATER
WASTEWATER
WASHOUTS
ADDITIVES
4 ROLL MILL
MIXER
PLODDER
SCRUBBER
WATER
WASTEWATER
WASHOUTS
CUTTER
PRESS
WRAPPER
SCRAP TO SOAP RECYCLE
FINISHED SOAP BARS AND CAKES TO WAREHOUSE
WASHOUTS

LIQUID SOAP PROCESSING (H)

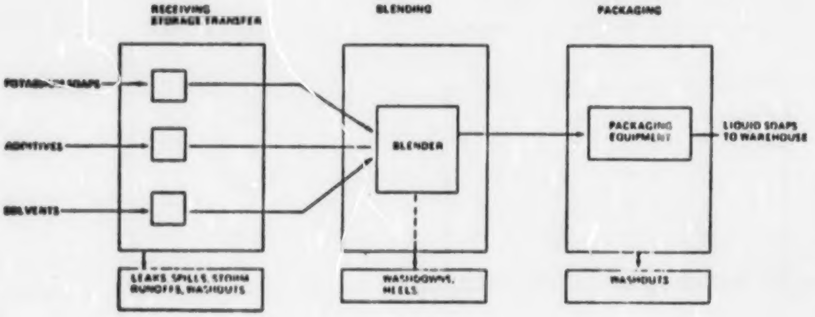

RECEIVING STORAGE TRANSFER
BLENDING
PACKAGING
POTASSIUM SOAPS
ADDITIVES
SOLVENTS
BLENDER
PACKAGING EQUIPMENT
LIQUID SOAPS TO WAREHOUSE
LEAKS, SPILLS, STORM RUNOFFS, WASHOUTS
WASHDOWNS, HEELS
WASHOUTS

FIGURE 8-13-4
PRODUCTION OF FINISHED SOAPS PROCESS FLOW DIAGRAMS

Flakes and Powders (F) - Neat soap may or may not be blended with other products before flaking or powdering. Neat soap is sometimes filtered to remove gel particles and run into a crutcher for mixing with builders. After thorough mixing, the finished formulation is run through various mechanical operations to produce flakes and powders. Since all of the evaporated moisture goes to the atmosphere, there is no wastewater effluent.

Some operations will include a scrap soap reboil to recover reclaimed soap. The soap reboil is salted out for soap recovery and the salt water is recycled. After frequent recycling the salt water becomes so contaminated that it must be discharged to the sewer.

Occasional washdown of the crutcher may be needed. The tower is usually cleaned down dry. There is also some gland water which flows over the pump shaft, picking up any minor leaks. This will contribute a very small, but finite, effluent loading.

There are a number of possible effluents shown on the flow diagrams for Process F. However, survey of the industry showed that most operating plants either recycled any wastewater to extinction or used dry clean-up processes. Occasionally, water will be used for clean-up.

Bar Soaps (G) - The procedure for bar soap manufacture (G) will vary significantly from plant to plant, depending upon the particular clientele served.

The amount of water used in bar soap manufacture varies greatly. In many cases, the entire bar soap processing operation is done without generating a single wastewater stream. The equipment is all cleaned dry, without any washups. In other cases, due to housekeeping requirements associated with the particular bar soap processes, there are one or more wastewater streams from air scrubbers.

The major waste streams in bar soap manufacture are the filter backwash, scrubber waters or condensate from a vacuum drier and water from equipment washdown. The main contaminant of all these streams is soap which will contribute primarily to BOD_5 and COD.

Liquid Soap (H) - In the making of liquid soap, neat soap (often the potassium soap of fatty acids) is blended in a mixing tank with other ingredients such as alcohols or glycols to produce a finished product, or the pine oil and kerosene for a product with greater solvency and versatility. The final blended product may be, and often is, filtered to achieve a sparkling clarity before being drummed. In making liquid soap, water is used to wash out the filter press and other equipment. According to manufacturers, there are very little effluent leaks. Spills can be recycled or handled dry. Washout between batches is usually unnecessary or can be recycled to extinction.

Detergent Manufacturing and Processing

Detergents can be formulated with a variety of organic and inorganic chemicals depending upon the cleaning characteristics desired. There are four main groups of detergents:

Anionics	Amphoterics
Cationics	Nonionics

Anionics comprise the most important group of detergents. They are usually the sodium salts of an organic sulfate or sulfonate of animal or petroleum origin.

Cationic detergents are known as "inverted soaps" and are produced in quite small volumes. They are relatively expensive and somewhat harsh on the skin. They make excellent bacteriostats and fabric softeners and are used for this purpose.

Nonionic detergents are an increasingly popular active ingredient of automatic washing machine formulations. These products are effective in hard water and are very low foamers. They are made by the addition of ethylene oxide to an alcohol.

Amphoterics are those detergents which can be either anionic or cationic, depending upon the pH of the system wherein they work. They account for only a small portion of the detergent market.

A finished, packaged detergent customarily consists of two main components - the active ingredient (surfactant) and the builder. The surfactant acts as the cleaning agent while the builder performs such functions as buffering the pH, soil dispersion, and antisoil redeposition. The processes described will include the manufacture of the surfactant as well as the preparation of the finished detergent.

Production of the surfactant is generally a two-step process:

- Sulfation or sulfonation
- Neutralization

Refer to flow diagram 8-13-1.

Oleum Sulfonation/Sulfation (I) - One of the most important active ingredients of detergents is the sulfate or sulfonate compounds made via the oleum route. A process flow diagram is shown in Figure 8-13-5. In most cases the sulfonation/sulfation is carried out continuously in a reactor where the oleum (a solution of sulfur trioxide in sulfuric acid) is brought into intimate contact with the hydrocarbon or alcohol. Reaction is rapid. The stream is then mixed with water where the surfactant separates out and is then sent to a settler. The spent acid is drawn off and usually sent for reprocessing, and the sulfonated/sulfated material is sent to be neutralized.

This process is normally operated continuously and performs indefinitely without need of periodic cleanout. A stream of water is generally played over pump shafts to pick up leaks as well as to cool the pumps. Wastewater flow from this source is quite modest but continual.

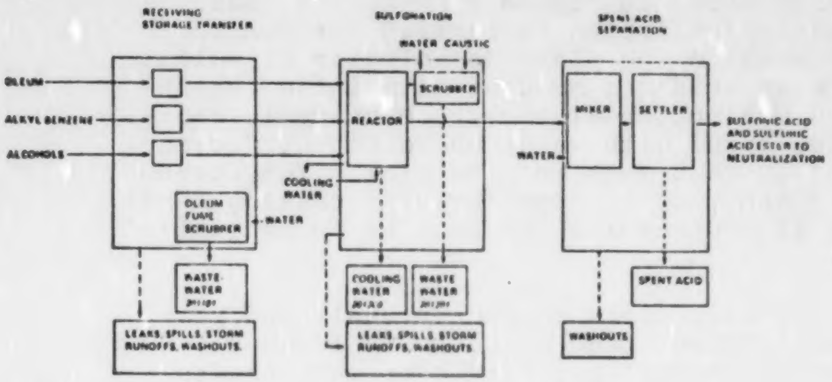
Air - SO_3 Sulfation/Sulfonation (J) - This process for surfactant manufacture has many advantages and is used extensively. With SO_3 sulfation, no water is generated in the reaction. A process flow diagram is shown in Figure 8-13-5. SO_3 can be generated at the plant by burning sulfur or sulfur dioxide with air instead of obtaining it as a liquid.

Because of this reaction's particular tendency to char the product, the reactor system must be cleaned thoroughly on a regular basis. In addition, there are usually several airborne sulfonic acid streams which must be scrubbed, with the wastewater going to the sewer during sulfation.

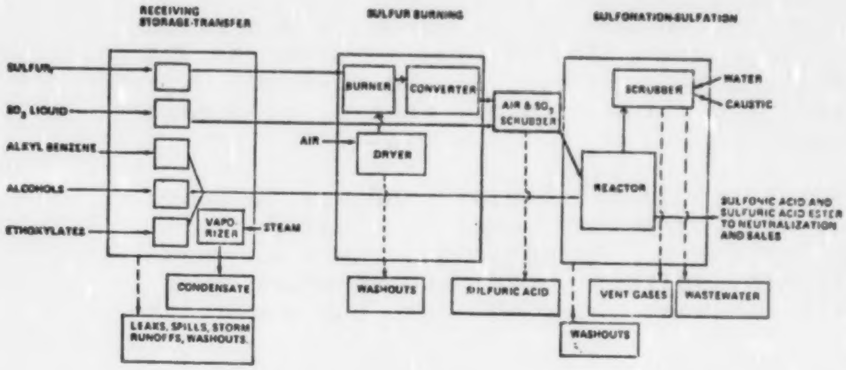
SO_3 Solvent and Vacuum Sulfonation (K) - Undiluted SO_3 and organic reactant are fed into the vacuum reactor through a mixing nozzle. A process flow diagram is shown in Figure 8-13-5. This system produces a high quality product. Offsetting this is the high operating cost of maintaining the vacuum. Other than occasional washout, the process is essentially free of wastewater generation.

Sulfamic Acid Sulfation (L) - Sulfamic acid is a mild sulfating agent and is used only in very specialized quality areas because of the high reagent price. A process flow diagram is shown in Figure 8-13-6. Washouts are the only wastewater effluents from this process.

OLEUM SULFATION AND SULFONATION (BATCH AND CONTINUOUS) (I)


RECEIVING
STORAGE TRANSFER
SULFONATION
SPENT ACID
SEPARATION
WATER
CAUSTIC
OLEUM
ALKYL BENZENE
ALCOHOLS
REACTOR
SCRUBBER
MIXER
SETTLER
SULFONIC ACID AND SULFURIC ACID ESTER TO NEUTRALIZATION
WATER
COOLING WATER
OLEUM FUME SCRUBBER
WATER
WASTE-WATER
COOLING WATER
WASTE WATER
SPENT ACID
LEAKS, SPILLS, STORM RUNOFFS, WASHOUTS.
LEAKS, SPILLS, STORM RUNOFFS, WASHOUTS
WASHOUTS

AIR–SO_3 SULFATION AND SULFONATION (BATCH AND CONTINUOUS) (J)


RECEIVING
STORAGE-TRANSFER
SULFUR BURNING
SULFONATION-SULFATION
SULFUR
SO3 LIQUID
ALKYL BENZENE
ALCOHOLS
ETHOXYLATES
VAPO-RIZER
STEAM
BURNER
CONVERTER
AIR
DRYER
AIR & SO3 SCRUBBER
SCRUBBER
WATER
CAUSTIC
REACTOR
SULFONIC ACID AND SULFURIC ACID ESTER TO NEUTRALIZATION AND SALES
CONDENSATE
LEAKS, SPILLS, STORM RUNOFFS, WASHOUTS.
WASHOUTS
SULFURIC ACID
VENT GASES
WASTEWATER
WASHOUTS

SO_3 SOLVENT AND VACUUM SULFONATION (K)

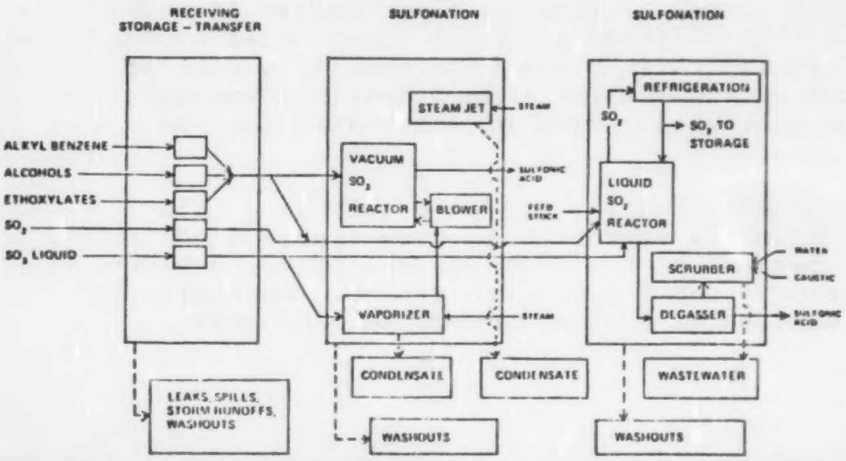
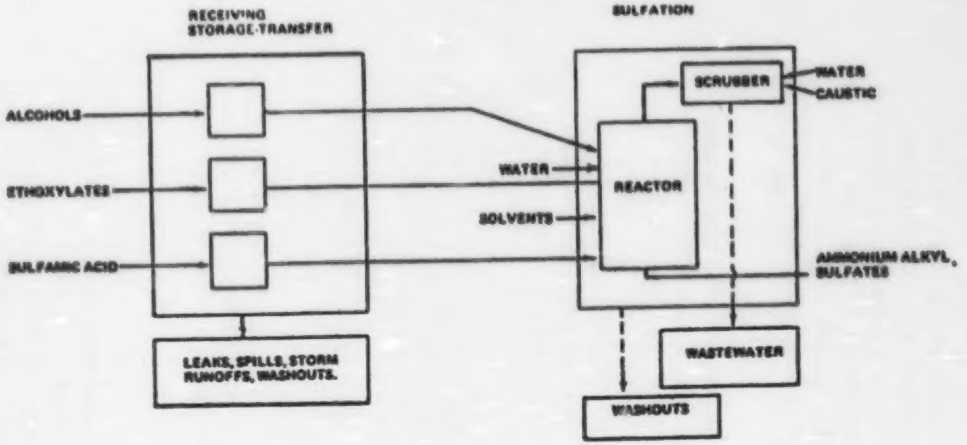

RECEIVING
STORAGE – TRANSFER
SULFONATION
SULFONATION
ALKYL BENZENE
ALCOHOLS
ETHOXYLATES
SO3
SO3 LIQUID
STEAM JET
STEAM
VACUUM SO3 REACTOR
BLOWER
SULFONIC ACID
VAPORIZER
STEAM
REFRIGERATION
SO2
SO2 TO STORAGE
FEED STOCK
LIQUID SO2 REACTOR
SCRUBBER
WATER
CAUSTIC
DEGASSER
SULFONIC ACID
CONDENSATE
CONDENSATE
WASTEWATER
LEAKS, SPILLS, STORM RUNOFFS, WASHOUTS
WASHOUTS
WASHOUTS

FIGURE 8-13-5
SULFATION AND SULFONATION BY THREE DIFFERENT PROCESSES

SULFAMIC ACID SULFATION (L)


RECEIVING
STORAGE-TRANSFER
SULFATION
ALCOHOLS
ETHOXYLATES
SULFAMIC ACID
WATER
SOLVENTS
REACTOR
SCRUBBER
WATER
CAUSTIC
AMMONIUM ALKYL,
SULFATES
LEAKS, SPILLS, STORM
RUNOFFS, WASHOUTS.
WASTEWATER
WASHOUTS

CHLOROSULFONIC ACID SULFATION (H)

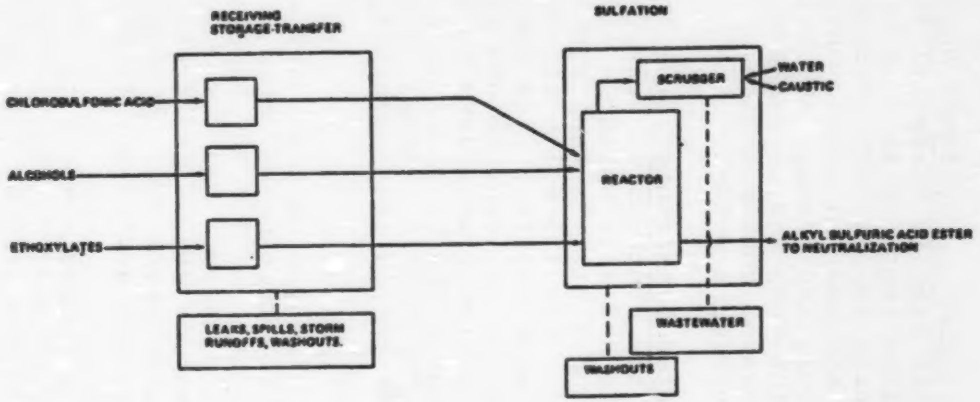

RECEIVING
STORAGE-TRANSFER
SULFATION
CHLOROSULFONIC ACID
ALCOHOLS
ETHOXYLATES
REACTOR
SCRUBBER
WATER
CAUSTIC
ALKYL SULFURIC ACID ESTER
TO NEUTRALIZATION
LEAKS, SPILLS, STORM
RUNOFFS, WASHOUTS.
WASTEWATER
WASHOUTS

FIGURE 8-13-6
SULFATION BY TWO DIFFERENT PROCESSES

Chlorosulfonic Acid Sulfation (M) - For products requiring high quality sulfates, chlorosulfonic acid is an excellent agent. It is a corrosive agent and generates hydrochloric acid as a by-product. A process flow diagram is shown in Figure 8-13-6. The effluent washouts are minimal.

Neutralization of Sulfuric Acid Esters and Sulfonic Acids (N) - This step is essential in the manufacture of detergent active ingredients. It converts the sulfonic acids or sulfuric acid esters (products produced by processes I - M) into neutral surfactants. It is a potential source of some cil and grease. Occasional leaks and spills around the pump and valves are the only expected source of wastewater contamination. A process flow diagram is shown in Figure 8-13-7.

Spray-Dried Detergents (O) - In this segment of the processing, the neutralized sulfonates and/or sulfates are first blended with builders and additives in the crutcher. The slurry is then pumped to the top of a spray tower of about 4.5-6.1 m (15-20 ft.) in diameter by 45-61 m (150-200 ft.) high where nozzles spray out detergent slurry. A large volume of hot air enters the bottom of the tower and rises to meet the falling detergent. The design preparation of this step will determine the detergent particle's shape, size and density, which in turn, determines its solubility rate in the washing process.

The air coming from the tower will be carrying dust particles which must be scrubbed, thus generating a wastewater stream. The spray towers are periodically shut down and cleaned. The tower walls are scraped and thoroughly washed down. The final step is mandatory since the manufacturers must be very careful to avoid contamination to the subsequent formulation.

Wastewater streams are rather numerous. (See flow diagram Figure 8-13-8. They include many washouts of equipment from the crutchers to the spray tower itself. One wastewater flow which has high loadings is that of the air scrubber which cleans and cools the hot gases existing from this tower.

All of the plants recycle some of the wastewater generated. Some of the plants recycle all of the flows generated.

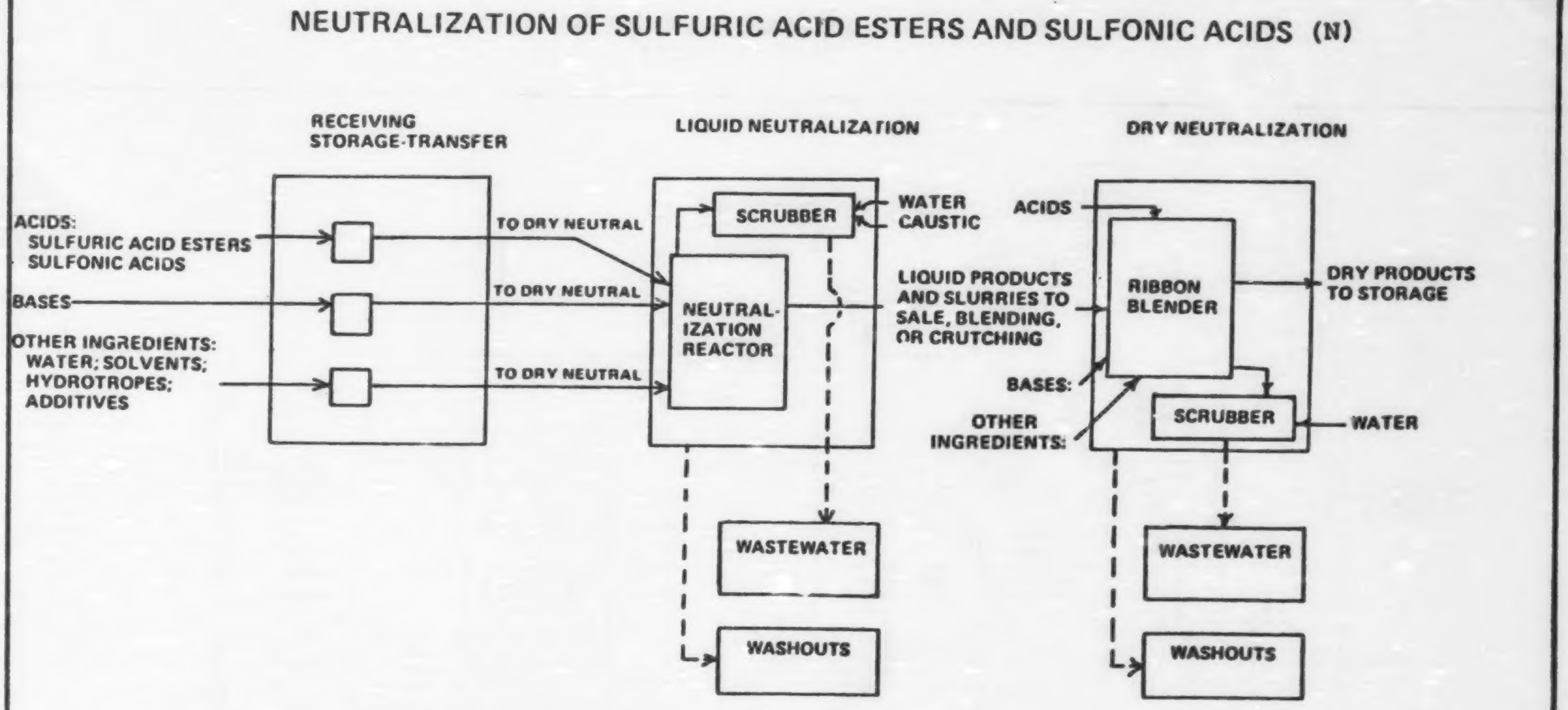

NEUTRALIZATION OF SULFURIC ACID ESTERS AND SULFONIC ACIDS (N)
RECEIVING STORAGE-TRANSFER
LIQUID NEUTRALIZATION
DRY NEUTRALIZATION
ACIDS: SULFURIC ACID ESTERS SULFONIC ACIDS
BASES
OTHER INGREDIENTS: WATER; SOLVENTS; HYDROTROPES; ADDITIVES
TO DRY NEUTRAL
TO DRY NEUTRAL
TO DRY NEUTRAL
SCRUBBER
NEUTRALIZATION REACTOR
WATER
CAUSTIC
LIQUID PRODUCTS AND SLURRIES TO SALE, BLENDING, OR CRUTCHING
WASTEWATER
WASHOUTS
ACIDS
BASES:
OTHER INGREDIENTS:
RIBBON BLENDER
DRY PRODUCTS TO STORAGE
SCRUBBER
WATER
WASTEWATER
WASHOUTS

FIGURE 8-13-7
NEUTRALIZATION OF SULFURIC ACID ESTERS
AND SULFONIC ACIDS

SPRAY DRIED DETERGENTS (O)

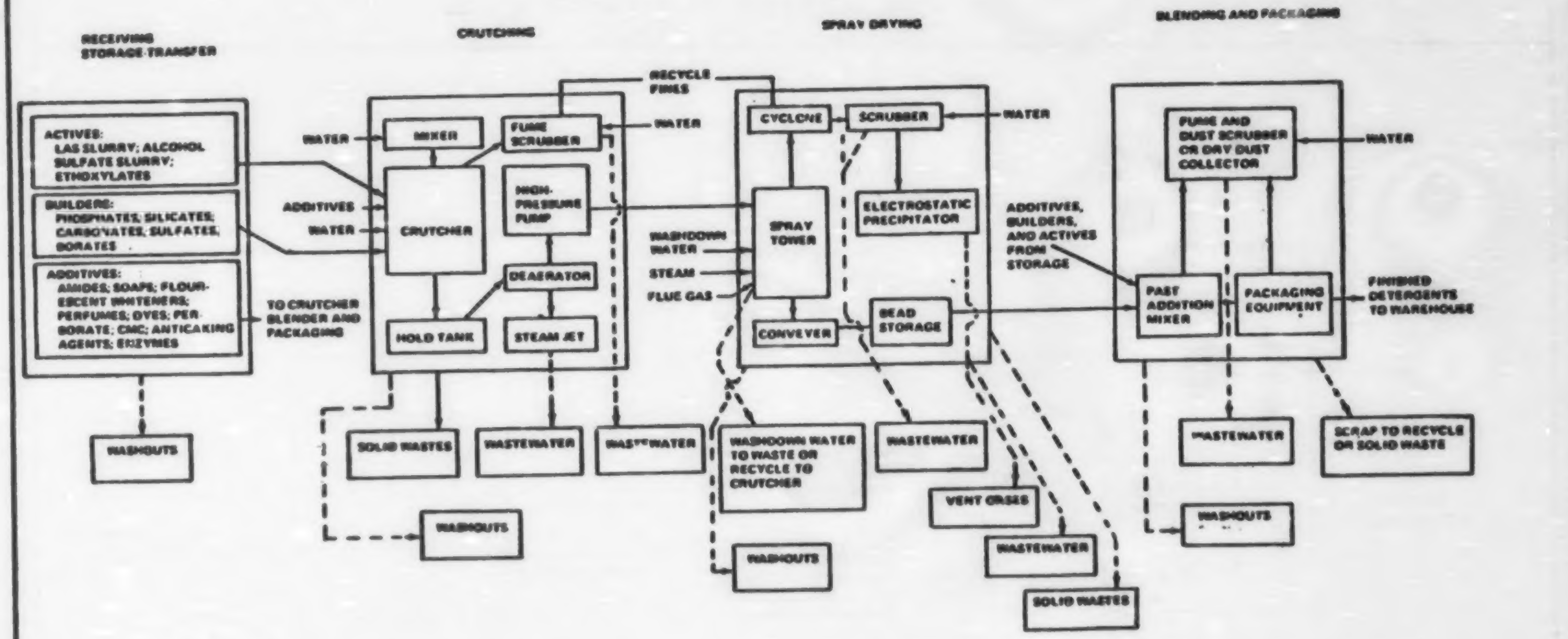

RECEIVING
STORAGE-TRANSFER
CRUTCHING
SPRAY DRYING
BLENDING AND PACKAGING
ACTIVES:
LAS SLURRY; ALCOHOL SULFATE SLURRY; ETHOXYLATES
BUILDERS:
PHOSPHATES; SILICATES; CARBONATES; SULFATES; BORATES
ADDITIVES:
AMIDES; SOAPS; FLOURESCENT WHITENERS; PERFUMES; DYES; PERBORATE; CMC; ANTICAKING AGENTS; ENZYMES
WASHOUTS
WATER
ADDITIVES
WATER
TO CRUTCHER BLENDER AND PACKAGING
MIXER
CRUTCHER
HOLD TANK
FUME SCRUBBER
HIGH-PRESSURE PUMP
DEAERATOR
STEAM JET
WATER
RECYCLE FINES
SOLID WASTES
WASTEWATER
WASTEWATER
WASHOUTS
WASHDOWN WATER
STEAM
FLUE GAS
CYCLONE
SCRUBBER
WATER
SPRAY TOWER
ELECTROSTATIC PRECIPITATOR
CONVEYER
BEAD STORAGE
WASHDOWN WATER TO WASTE OR RECYCLE TO CRUTCHER
WASTEWATER
VENT GASES
WASTEWATER
SOLID WASTES
WASHOUTS
ADDITIVES, BUILDERS, AND ACTIVES FROM STORAGE
FUME AND DUST SCRUBBER OR DRY DUST COLLECTOR
WATER
PAST ADDITION MIXER
PACKAGING EQUIPMENT
FINISHED DETERGENTS TO WAREHOUSE
WASTEWATER
SCRAP TO RECYCLE OR SOLID WASTE
WASHOUTS

FIGURE 8-13-8
SPRAY DRIED DETERGENTS

Due to increasingly stringent air quality requirements, we can expect that fewer plants will be able to maintain a complete recycle system of all water flows in the spray tower area.

After the powder comes from the spray tower it is further blended and then packaged.

Liquid Detergents (P) - Detergent actives are pumped into mixing tanks where they are blended with numerous ingredients, ranging from perfumes to dyes. A process flow diagram is shown in Figure 8-13-9. From here, the fully formulated liquid detergent is run down to the filling line for filling, capping, labeling, etc. Whenever the filling line is to change to a different product, the filling system must be thoroughly cleaned out to avoid cross contamination.

Dry Detergent Blending (Q) - Fully dried surfactant materials are blended with additives in dry mixers. Normal operation will see many succeeding batches of detergent mixed in the same equipment without anything but dry cleaning. However, when a change in formulation occurs, the equipment must be completely washed down. A modest amount of wastewater is generated. A process flow diagram is shown in Figure 8-13-9.

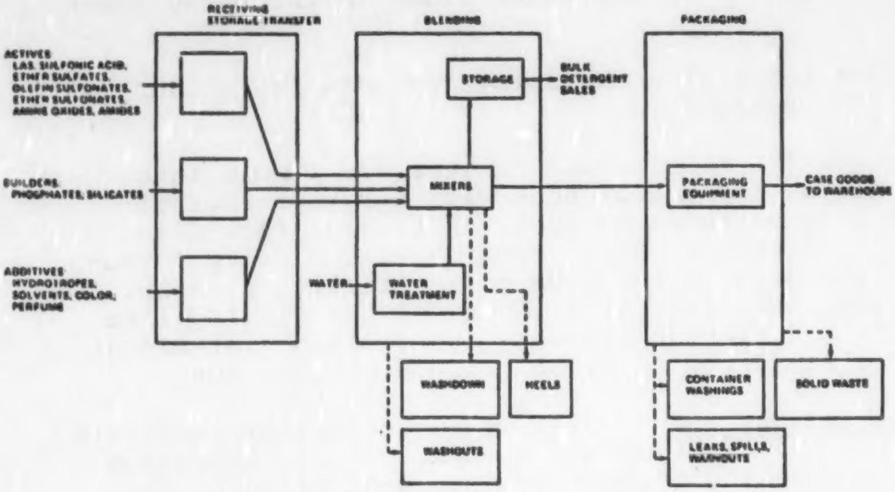
Drum Dried Detergents (R) - This process is one method of converting liquid slurry to a powder, and should be essentially free of generation of wastewater discharge other than occasional washdown. A process flow diagram is shown in Figure 8-13-9.

Detergent Bars and Cakes (S) - Detergent bars are either 100% synthetic detergent or a blend of detergent and soap. They are blended in essentially the same manner as that used for conventional soap. Fairly frequent cleanups generate a wastewater stream. A process flow diagram is shown in Figure 8-13-10.

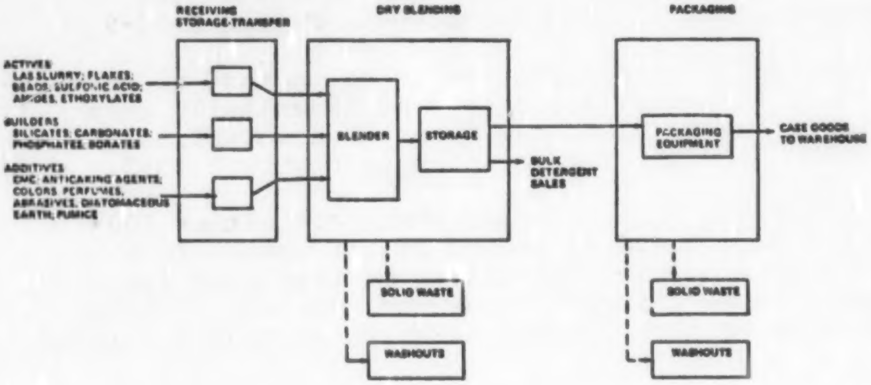
4. Wastewater Characteristics

Table 8-13-1 and 8-13-2 contain the characteristics of the wastewaters from the seventeen subcategories of the industry. Most plants contain two or several of the subcategories shown on the table and their wastewaters will be a composite of these individual unit processes.

LIQUID DETERGENT MANUFACTURE (P)


RECEIVING
STORAGE TRANSFER
BLENDING
PACKAGING
ACTIVES
LAS, SULFONIC ACID,
ETHER SULFATES,
OLEFIN SULFONATES,
ETHER SULFONATES
AMINE OXIDES, AMIDES
BUILDERS
PHOSPHATES, SILICATES
ADDITIVES
HYDROTROPES,
SOLVENTS, COLOR,
PERFUME
STORAGE
BULK
DETERGENT
SALES
MIXERS
WATER
WATER
TREATMENT
PACKAGING
EQUIPMENT
CASE GOODS
TO WAREHOUSE
WASHDOWN
HEELS
WASHOUTS
CONTAINER
WASHINGS
SOLID WASTE
LEAKS, SPILLS,
WASHOUTS

DETERGENT MANUFACTURE BY DRY BLENDING (Q)


RECEIVING
STORAGE-TRANSFER
DRY BLENDING
PACKAGING
ACTIVES
LAS SLURRY; FLAKES;
BEADS; SULFONIC ACID;
AMIDES, ETHOXYLATES
BUILDERS
SILICATES; CARBONATES;
PHOSPHATES; BORATES
ADDITIVES
CMC; ANTICAKING AGENTS;
COLORS, PERFUMES,
ABRASIVES, DIATOMACEOUS
EARTH; PUMICE
BLENDER
STORAGE
BULK
DETERGENT
SALES
PACKAGING
EQUIPMENT
CASE GOODS
TO WAREHOUSE
SOLID WASTE
WASHOUTS
SOLID WASTE
WASHOUTS

DRUM DRIED DETERGENT (R)

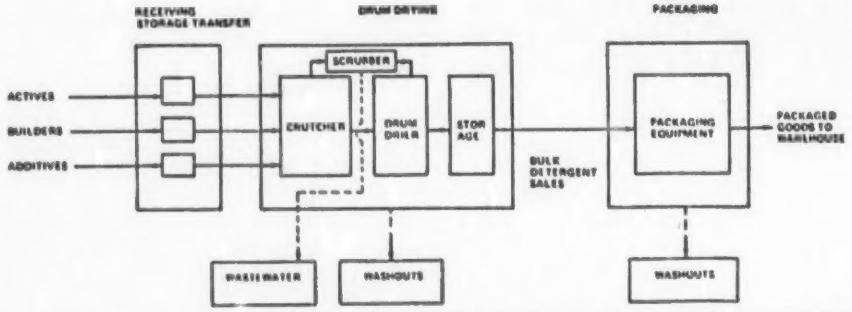

RECEIVING
STORAGE TRANSFER
DRUM DRYING
PACKAGING
ACTIVES
BUILDERS
ADDITIVES
SCRUBBER
CRUTCHER
DRUM
DRIER
STOR
AGE
BULK
DETERGENT
SALES
PACKAGING
EQUIPMENT
PACKAGED
GOODS TO
WAREHOUSE
WASTEWATER
WASHOUTS
WASHOUTS

FIGURE 8-13-9
DETERGENT MANUFACTURE

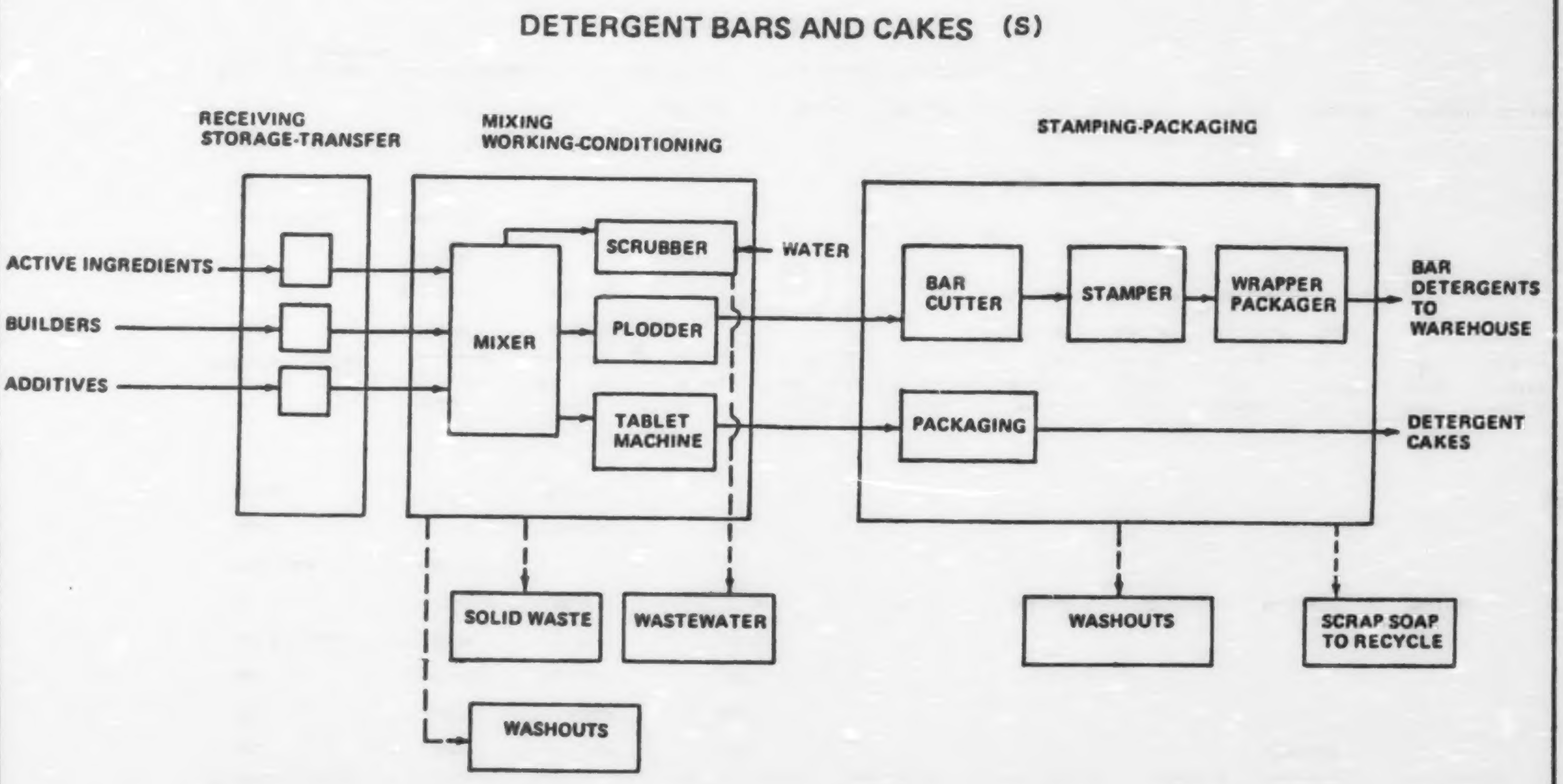

DETERGENT BARS AND CAKES (S)
RECEIVING STORAGE-TRANSFER
MIXING WORKING-CONDITIONING
STAMPING-PACKAGING
ACTIVE INGREDIENTS
BUILDERS
ADDITIVES
MIXER
SCRUBBER
WATER
PLODDER
TABLET MACHINE
BAR CUTTER
STAMPER
WRAPPER PACKAGER
BAR DETERGENTS TO WAREHOUSE
PACKAGING
DETERGENT CAKES
SOLID WASTE
WASTEWATER
WASHOUTS
WASHOUTS
SCRAP SOAP TO RECYCLE

FIGURE 8-13-10
DETERGENT BARS AND CAKES

TABLE 8-13-1
SOAP AND DETERGENTS INDUSTRY
RAW WASTEWATER CHARACTERISTICS

Parameter (mg/l)	Batch Kettle A	Fat Splitting B	Fatty Acid Neutralization C	Glycerine Concentration D	Glycerine Distillation E	Flakes & Powders F	Bar Soap G	Liquid Soap H
BOD	3600*	60-3600*	400				1600-3000*	
COD	4267*	115-6000*	1000					
TSS	1600-6420	115-6000	775					
Oil & Grease	250*	13-760*	200*					
pH	5-13.5	High	High	Neutral	Neutral	Neutral	Neutral	Neutral
Chlorides	20M*-47M*							
Zinc		Present						
Nickel		Present						

Parameter (mg/l)	Oleum Sul & Sul I	Air Sul & Sul J	SO_3 Sol & Vac K	Sulfamic Acid Sol. L	Chloro-Sulfonic M	Neutral Sulfuric N	Spray Dried O	Liquid Det. P	Dry Blend Q	Drum Dried R	Bars & Cakes S
BOD	75-2000*	380-520				8.5-6M*	48-19M*	65-3400*	Neg.		
COD	220-6000*	920-1589*				245-21M*	150-60M*	640-11M*			
TSS	100-3000										
Oil & Grease	100-3000*										
pH	1-2*	2*-7	Low	Low	Low	Low					
Surfactant	250-7900							60-2M			
Boron	Present	Present	Present	Present	Present	Present	Present	Present	Present	Present	Present

Note: * See Appendix 5 for parameters which may be inhibitory to biological systems.
M - Thousand

TABLE 8-13-2
SOAP AND DETERGENTS INDUSTRY
RAW WASTEWATER CHARACTERISTICS BASED UPON PRODUCTION

Parameter	Batch Kettle A	Fat Splitting B	Fatty Acid Neut. C	Glycerine Concentration D	Glycerine Distillation E	Flakes & Powders F	Bar Soap G	Liquid Soap H
Flow Range(l/kkg)[1]	623/2900	3.3M/192M	258			Neg.		Neg.
Flow Type	B	B	B	B	B	B	B	B
BOD (kg/kkg)[2]	6	12	0.1	15	5	0.1	3.4	0.1
COD (kg/kkg)	10	22	.25	30	10	.3	5.7	.3
TSS (kg/kkg)	4	22	.2	2	2	.1	5.8	.1
Oil & Grease (kg/kkg)	.9	2.5	.05	1	1	.1	.4	.1

Parameter	Oleum Sul & Sul I	SO_3 Sul & Sul J	SO_3 Sol & Vac. Sul K	Sulfamic Acid Sul L	Chlorosulfonic Acid Sul M	Neutral Sulfuric Acid Esters N	Spray Dried O	Liquid Det. P	Dry Blend Q	Drum Dried R	Bars & Cakes S
Flow Range(l/kkg)[1]	100/2740	249				10/4170	41/2084	625/6250			
Flow Type	C	C	B	B	B	B&C	B	B	B	B	B
BOD (kg/kkg)[2]	.2	3	3	3	3	.10	.1-.8	2-5	.1	.1	7
COD (kg/kkg)	.6	9	9	9	9	.3	.3-25	4-7	.5	.3	22
TSS (kg/kkg)	.3	.3	.3	.3	.3	.3	.1-1.0		.1	.1	2
Oil & Grease (kg/kkg)	.3	.5	.5	.5	.5	.1	Nil-.3			.1	.2
Chloride (kg/kkg)					5						
Surfactant (kg/kkg)	.7	3	3	3	3	.2	.2-1.5	1.3-3.3		.1	5

Note: [1] l/kkg liters/1000 kg product produced (lower limit/upper limit)
[2] kg/kkg kilograms per 1000 kilograms of product produced
B - Batch
C - Continuous
Neg - Negligible
M - Thousand

5. Control and Treatment Technology

In-Plant Control

Significant in-plant control of both waste quantity and quality is possible particularly in the soap manufacturing subcategories where maximum flows may be 100 times the minimum. Considerably less in-plant water conservation is possible in the detergent industry where flows per unit of product are smaller.

The largest in-plant modification that could be made is the changing or replacement of the barometric condensers (processes A, B, D, E). The quantity of wastes discharged from these processes could be significantly reduced by recycling the barometric cooling water through fat skimmers from which valuable fats and oils could be recovered and then through the cooling towers. The only waste with this type of cooling would be the continuous small blowdown from the skimmer. Replacement with surface condensers has been used in several plants to reduce both the waste flow and the quantity of organics wasted.

Significant reduction of water usage is possible in the manufacture of liquid detergents (P) by the installation of water recycle piping and tankage and by the use of air rather than water to blowdown filling lines.

In the production of bar soaps (G), the volume of discharge and the level of contamination can be reduced materially by installation of an atmospheric flash evaporator ahead of the vacuum drier.

Pollutant carry-over from distillation columns such as those used in glycerine concentration (D) or fatty acid separation (B) can be reduced by the use of two additional special trays.

Treatment Technology

The industry routinely utilizes a broad range of pretreatment processes in control of its effluent. The treatment methods used are shown in Table 8-13-3. Also shown in this table are the anticipated removal efficiencies of the processes on the various pollutants generated. A composite flow sheet showing a complete treatment system for the soap and detergent industry is shown in Figure 8-13-11. As a minimum, even small plants with batch operations should employ equalization to smooth out peak discharges. Larger plants with an

Table 8-13-3
Treatment Methods Used in the Soap and Detergent Industry

Pollutant and Method	Efficiency (Percentage of Pollutant Removed)
Oil and Grease	
API type separation	Up to 90 percent of free oils and greases. Variable on emulsified oil.
Carbon adsorption	Up to 95 percent of both free and emulsified oils.
Flotation	Without the addition of solid phase, alum or iron, 70-80 percent of both free and emulsified oil. With the addition of chemicals, 90 percent
Mixed media filtration	Up to 95 percent of free oils. Efficiency in removing emulsified oils unknown.
Coagulation-sedimentation with iron, alum or solid phase (bentonite, etc.)	Up to 95 percent of free oil. Up to 90 percent of emulsified oil.
Suspended Solids	
Mixed media filtration	70-80 percent
Coagulation-sedimentation	50-80 percent
BOD and COD	
Bioconversions (with final clarifier)	60-95 percent or more
Carbon adsorption	Up to 90 percent
Residual Suspended Solids	
Sand or mixed media filtration	50-95 percent
Dissolved Solids	
Ion exchange or reverse osmosis	Up to 90 percent

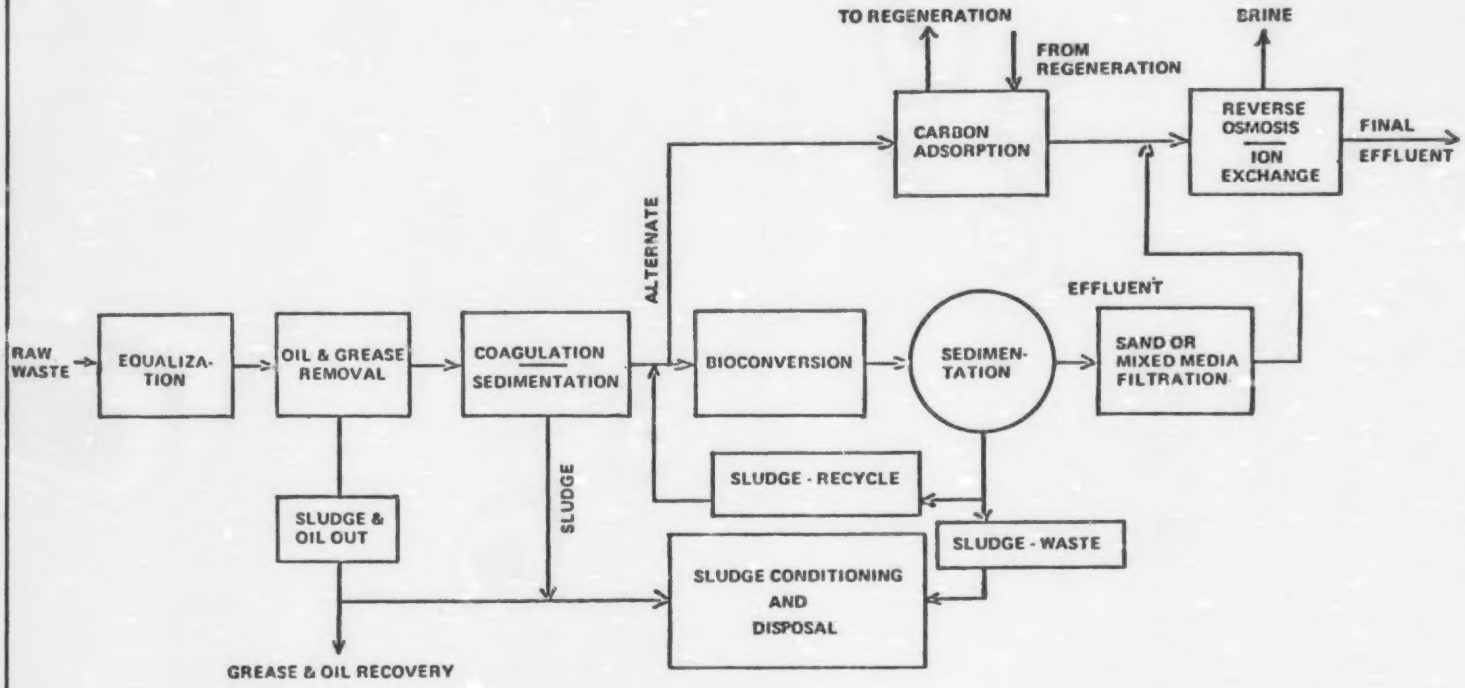

RAW WASTE
EQUALIZA-TION
OIL & GREASE REMOVAL
SLUDGE & OIL OUT
GREASE & OIL RECOVERY
COAGULATION
SEDIMENTATION
SLUDGE
ALTERNATE
BIOCONVERSION
SLUDGE - RECYCLE
SLUDGE CONDITIONING AND DISPOSAL
SEDIMEN-TATION
SLUDGE - WASTE
EFFLUENT
SAND OR MIXED MEDIA FILTRATION
TO REGENERATION
FROM REGENERATION
CARBON ADSORPTION
BRINE
REVERSE OSMOSIS
ION EXCHANGE
FINAL EFFLUENT

FIGURE 8-13-11
COMPOSITE FLOW SHEET
WASTE TREATMENT
SOAP & DETERGENT INDUSTRY

integrated product line may require both suspended solids and organics removal in addition. The bulk of the large solid material in the industry's waste is removed by coagulation and sedimentation. Fine solid material can be removed by sand or mixed bed filtration applied as a tertiary step after biological oxidation. Organics removal is typically provided by either one of several forms of biological oxidation or by powdered or granulated activated carbon adsorption. A few plants employ reverse osmosis or ion exchange as a tertiary step for the removal of individual dissolved pollutants or TDS.

1. General Industry Description

This report describes the manufacture of fertilizer based on two of the three major plant nutrients: nitrogen, phosphate and mixtures of the two. The third basic nutrient, potassium, is not included.

The fertilizer industry produces the primary nutrient source for the nation's agricultural community. Many of its products are toxic to aquatic organisms and many are a direct hazard to man when in a concentrated form.

This industry includes Standard Industrial Classifications(SIC) 2873, 2874 and 2875.

2. Industrial Categorization

Nitrogen based fertilizers can create spectacular crop responses. Such response, however, is comparatively short lived and can result in disastrous crop failures unless nitrogen fertilization is followed with phosphate and potassium fertilization within one or two years. Figure 8-14-1 is a product manufacturing flow diagram for the nitrogen and phosphate fertilizer industry. The industry subcategorization along process lines is as follows:

Subcategory	Designation
Phosphate	A
Ammonia	B
Urea	C
Ammonium Nitrate	D
Nitric Acid	E
Ammonium Sulfate	F
Mixed and Blend Fetilizer	G

3. Process Description

Phosphate (A)

The phosphate fertilizer industry is defined as eight separate processes: phosphate rock grinding, wet process phosphoric acid, phosphoric acid concentration, phosphoric acid clarification, normal superphosphate, triple superphosphate, ammonium phosphate and sulfuric acid. Practically all phosphate manufacturers combine the various effluents into a large recycle water system. It is only when the quantity of recycle water increases beyond capacity to contain it, that effluent treatment is necessary.

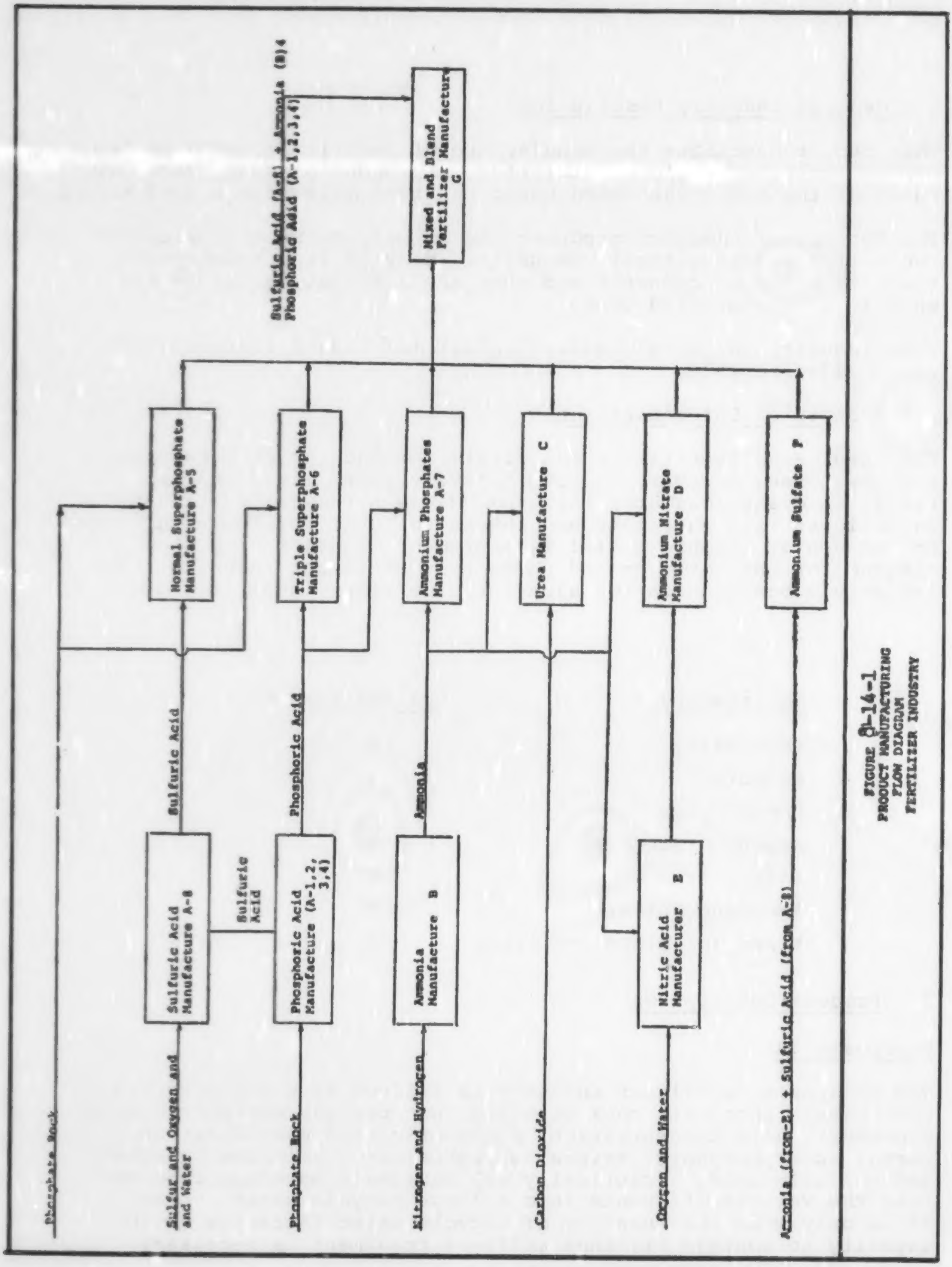

Phosphate Rock
Sulfur and Oxygen and and Water
Sulfuric Acid Manufacture A-8
Sulfuric Acid
Sulfuric Acid
Normal Superphosphate Manufacture A-5
Phosphate Rock
Phosphoric Acid Manufacture (A-1,2,3,4)
Phosphoric Acid
Triple Superphosphate Manufacture A-6
Nitrogen and Hydrogen
Ammonia Manufacture B
Ammonia
Ammonium Phosphates Manufacture A-7
Carbon Dioxide
Urea Manufacture C
Oxygen and Water
Nitric Acid Manufacturer E
Ammonium Nitrate Manufacture D
Ammonia (from-B) + Sulfuric Acid (from A-8)
Ammonium Sulfate F
Sulfuric Acid (A-8) + Ammonia (B) +
Phosphoric Acid (A-1,2,3,4)
Mixed and Blend Fertilizer Manufactur G

FIGURE 8-14-1
PRODUCT MANUFACTURING
FLOW DIAGRAM
FERTILIZER INDUSTRY

(1) Phosphate Rock Grinding

Phosphate rock is mined and mechanically ground to provide the optimum particle size required for phosphoric acid production. There are no liquid effluents.

(2) Wet Process Phosphoric Acid

A process flow diagram is shown in Figure 8-14-2. Insoluble phosphate rock is changed to the water soluble phosphoric acid by solubilizing the phosphate rock with an acid, generally sulfuric or nitric acid. The phosphoric acid produced from the nitric acid process is blended with other ingredients to produce a fertilizer. The phosphoric acid produced from the sulfuric acid process must be concentrated before further use. Minor quantities of fluorine, iron, aluminum, silica, and uranium are present in phosphate rock. Of these, fluorine presents the most serious effluent problem.

(3) Phosphoric Acid Concentration

Phosphoric acid produced with sulfuric acid is of too low a concentration to be used for processing. It is, therefore, concentrated by evaporation to the 40-54% concentration.

Waste streams will contain fluorine and phosphoric acid.

(4) Phosphoric Acid Clarification

When the phosphoric acid has been concentrated, iron and aluminum phosphates, gypsum and fluorosilicates become insoluble and can become problems during acid storage. They are therefore removed by clarification and/or centrifugation.

(5) Normal Superphosphate

Normal superphosphate is produced by the reaction between ground phosphate rock and sulfuric acid followed by a three to eight week curing time. Obnoxious gases are generated.

(6) Triple Superphosphate (TSP)

Triple superphosphate is produced by the reaction between ground phosphate rock and phosphoric acid by either of two processes. One utilizes concentrated phosphoric acid and generates obnoxious gases. The dilute phosphoric acid process permits ready collection of dusts and obnoxious gases.

(7) Ammonium Phosphate

Ammonium Phosphate, a concentrated water soluble plant food, is produced by reacting ammonia and phosphoric acid. The resultant slurry is dried, stored and shipped.

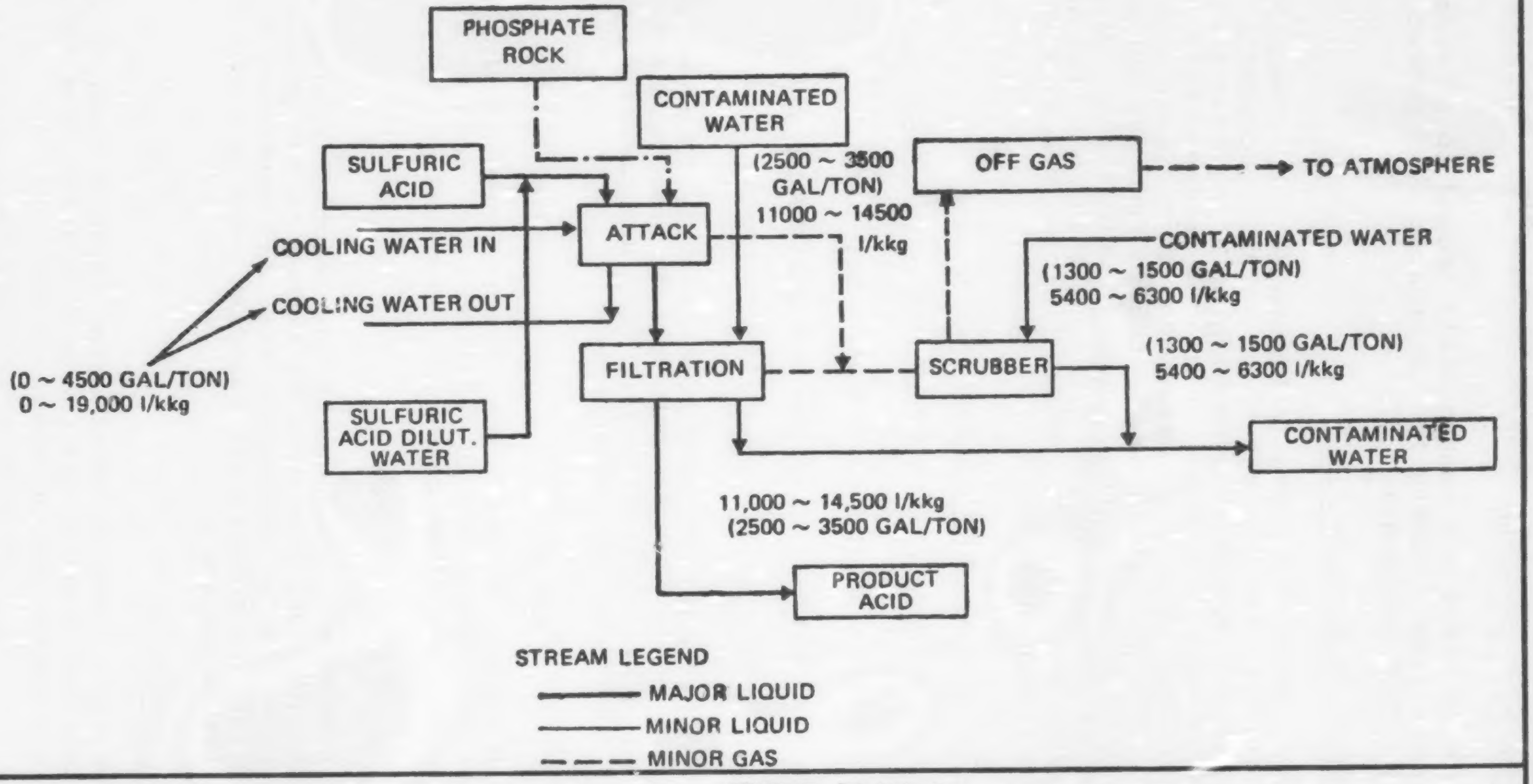

PHOSPHATE ROCK
CONTAMINATED WATER
SULFURIC ACID
(2500 ~ 3500 GAL/TON) 11000 ~ 14500 l/kkg
OFF GAS
TO ATMOSPHERE
ATTACK
CONTAMINATED WATER
COOLING WATER IN
(1300 ~ 1500 GAL/TON) 5400 ~ 6300 l/kkg
COOLING WATER OUT
(1300 ~ 1500 GAL/TON) 5400 ~ 6300 l/kkg
FILTRATION
SCRUBBER
(0 ~ 4500 GAL/TON) 0 ~ 19,000 l/kkg
SULFURIC ACID DILUT. WATER
CONTAMINATED WATER
11,000 ~ 14,500 l/kkg (2500 ~ 3500 GAL/TON)
PRODUCT ACID
STREAM LEGEND
MAJOR LIQUID
MINOR LIQUID
MINOR GAS

FIGURE 8-14-2

WET PROCESS PHOSPHORIC ACID – H_2SO_4 ACIDULATION

FLOW RATE PER TON P_2O_5

(8) Sulfuric Acid

Essentially, all sulfuric acid manufactured in this industry is produced by the "contact" process. The name refers to the fact that sulfur dioxide (SO_2) and oxygen (O_2) contact each other on the surface of a catalyst (vanadium pentoxide) to form sulfur trioxide (SO_3) gas. Sulfur trioxide gas is added to water to form sulfuric acid (H_2SO_4). The sulfur dioxide is produced by burning elemental sulfur in a furnace.

In addition, the process is designed to capture a high percentage of the energy released by the exothermic chemical reactions occuring in the oxidation of sulfur to sulfur tioxide. This energy is used to produce steam which is then utilized for other plant unit operations or converted to electrical energy. It is the raw water treatment necessary to condition water for this steam production that generates essentially all the water effluent from this process.

Ammonia (B)

Ammonia, the base component for the nitrogen fertilizer industry, is produced by reacting nitrogen with hydrogen at elevated pressure in the presence of a catalyst. The ammonia plant may include a complex gas preparation operation to provide feedstock to the ammonia synthesis section. The raw material source of nitrogen is air. Hydrogen is available from a variety of sources including refinery off-gas and reforming of methane. This process generates wastewaters containing ammonia, methanol, organics and trace metals.

Urea (C)

Urea is produced by reacting carbon dioxide with ammonia at high pressures and temperatures. After separation of the ammonia from the unreacted components it is either sold or further concentrated.

Ammonium Nitrate (D)

Ammonium Nitrate is produced by reacting ammonia with nitric acid. The high heat of reaction causes flash vaporization which can be an air pollution problem, or if condensed, can cause a water pollution problem.

Nitric Acid (E)

Nitric acid is produced by the ammonia oxidation process. Ammonia is first reacted with air to produce oxides of nitrogen which are then further oxidized and absorbed in water producing 55-65% nitric acid. There are no waste streams from this process.

Ammonium Sulfate (F)

Ammonium sulfate is produced by neutralizing sulfuric acid with ammonia. This product may utilize virgin ammonia or it may be manufactured as a by-product in the coke making industry where ammonia is formed as an off-gas. Wastewaters are generally collected and recycled.

Mixed and Blend Fertilizer (G)

Mixed Fertilizer

The raw materials used to produce mixed fertilizer goods include inorganic acids, solutions, double nutrient fertilizers, and all types of straight fertilizers. The choice of raw materials is dependent on the specific nitrogen, phosphate, potassium (N-P-K) formulation to be produced and the cost of the different possible materials from which it can be made.

The Mixed Fertilizer process involves the controlled addition of both dry and liquid raw materials to a granulator. The granulator is normally a rotary drum, but pug mills are also used. Raw materials, plus some recycled product material are mixed to form an essentially homogeneous granular product. Wet granules from the granulator are discharged into a rotary drier where the excess water is evaporated. Dried granules from the drier are sized on vibrating screens. Over and under size granules are separated for use as recycle material in the granulator. Product size granules are cooled and conveyed to storage or shipping.

Blend Fertilizer

Raw materials are a combination of granular dry straight and mixed fertilizer materials with essentially identical particle size. While many materials can be utilized, the five most commonly used are ammonium nitrate, urea, triple superphosphate, diammonium phosphate, and potash. These raw materials are stored in a multi-compartmented bin and withdrawn in the precise quantities needed to produce the nitrogen-phosphorus-potassium (N-P-K) formulation desired. Raw material addition is normally by batch weighing. The combination of batch-weighed and granular raw materials are then conveyed to a mechanical blender for mixing. From the blender the product is conveyed to storage or shipping.

4. Wastewater Characteristics

Few fertilizer plants discharge to municipal treatment systems. When retention pond capacities in the phosphate industry are exceeded, the overflows are treated and discharged. Tables 8-14-1 and 8-14-2 contain the characteristics of the pond water in the phosphate subcategory and the recycle water in the other subcategories.

TABLE 8-14-1

Fertilizer Industry

Raw Wastewater Characteristics

Parameter	Phosphate A	Ammonia B	Urea C	Ammonium Nitrate D	Nitric Acid E	Ammonium Sulfate F	Mixed & Blend G
Suspended Solids (mg/l)	800-1200						
pH	1-2*						
Ammonia (mg/l)	450-500*	500-1200*	10M*	300-750*			
Sulfate (mg/l)	4000						
Chloride (mg/l)	58						
Total Phosphate (mg/l)	3M-5M						
Fluoride (mg/l)	6M-8.5M*						
Aluminum (mg/l)	110						
Iron (mg/l)	85						
Urea (mg/l)			40M	15M-35M			
Radium 226 (picocuries)	60-100						

Note: * See Appendix 5 for parameters which may be inhibitory to biological systems

M - Thousand

TABLE 8-14-2

Fertilizer Industry

Raw Wastewater Data Based Upon Production

Parameter	Phosphate A	Ammonia B	Urea C	Ammonium Nitrate D	Nitric Acid E	Ammonium Sulfate F	Mixed & Blend G
Flow (l/kkg)		3300/5500	417/935	208/458	None		
NH_3 (kg/kkg)		1200/1750	19,800	330			
Urea (kg/kkg)			73,700				
Ammonium Nitrate (kg/kkg)				15,400			

5. Control and Treatment Technology

Contaminated water from the phosphate subcateogry (A) can be collected in ponds and treated for control of pH, phosphorus and fluorides. Treatment is by means of a "double liming" or two stage neutralization procedure, in which fluorides and phosphates precipitate out.

Seepage collection and reimpoundment is accomplished by construction of a seepage collection ditch around the perimeter of the diked area and erection of a secondary dike.

The sulfuric acid plant will have boiler blowdown and cooling tower blowdown waste streams, which will be uncontaminated. However, accidental spills of acid can and do occur. When they occur, the spills will contaminate the blowdown streams. Therefore, neutralization facilities should be supplied for the blowdown waste streams.

Waste streams from the nitrogen fertilizer industry (B, C, D, F) can be recycled back to the process. There are no wastewaters from nitric acid production (E).

Mixed Fertilizer (G) treatment technology consists of a closed loop contaminated water system which includes a retention pond to settle suspended solids. The water is then recycled back to the system.

There are no liquid waste streams associated with the Blend Fertilizer (G) process except where liquid air scrubbers are used to prevent air pollution. Dry removals of air pollutants prevent a wastewater stream from being formed.

1. General Industry Description

The petroleum refining industry produces consumer goods such as propane, gasoline, jet fuels, heating oils, lubricating oils, asphalt, and coke. These materials are derived from crude oil by means of distillation, catalytic conversion, solvent extraction, and chemical conversion operations. This industry is covered by Standard Industrial Classification (SIC) 2911.

2. Industrial Categorization

The industry has been subcategorized along process lines and with a view toward delineating waste loads:

Subcategory	Designation
Topping	A
Cracking	B
Petrochemical	C
Lube	D
Integrated	E

3. Process Description

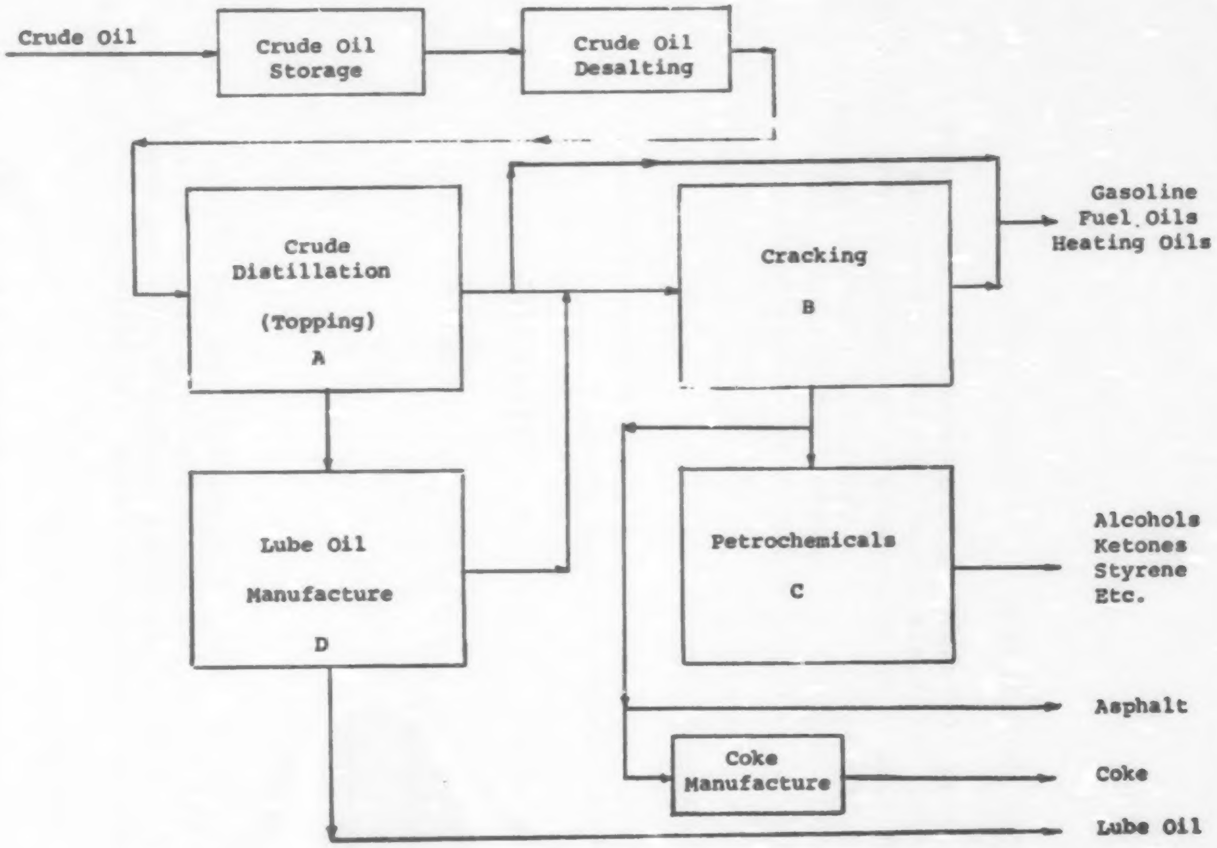
Figure 8-15-1 is a process flow diagram for the petroleum refining industry and shows the interrelationships among the five subcategories. Each subcategory includes various combinations of the process operations described below.

a. Crude Oil and Product Storage

The storage area of the refinery serves to provide a working supply, equalizes process flow and also acts as a place for separation of water and suspended solids from the crude oil. Wastewaters associated with storage of crude oil are high in oil, suspended solids and COD.

b. Crude Desalting

The crude oil desalting process is a pretreatment step to remove impurities. Wastewaters containing inorganic salts and suspended solids are discharged.


Crude Oil
Crude Oil Storage
Crude Oil Desalting
Crude Distillation (Topping) A
Cracking B
Gasoline
Fuel Oils
Heating Oils
Lube Oil Manufacture D
Petrochemicals C
Alcohols
Ketones
Styrene
Etc.
Asphalt
Coke Manufacture
Coke
Lube Oil

NOTE - Integrated subcategory, E, includes all of the processes shown.

Figure 8-15-1
Product Manufacturing Flow Diagram
Petroleum Refining

c. Crude Oil Fractionation

Fractionation is the basic refining process for the separation of crude petroleum into intermediate fractions of specified boiling point ranges. Wastewaters contain sulfides, ammonia, chlorides, mercaptans and phenols.

d. Cracking

In this process, heavy oil fractions are converted into lower molecular weight fractions including domestic heating oils, high octane gasoline stocks and furnace oils. Three types of cracking are used: Thermal, catalytic, and hydrocracking. Thermal cracking is accomplished by heating (480-603°C) without the use of a catalyst. Wastewaters usually contain oils and distillates, and are high in BOD, COD, ammonia, phenol, sulfides, and alkalinity.

Catalytic cracking is operated at lower temperatures and pressures than with thermal cracking because of the use of a catalyst. Catalytic cracking units are one of the largest sources of sour and phenolic wastewaters in a refinery. The major pollutants are oil, sulfides, phenols, cyanides, and ammonia. Regeneration of the catalyst may constitute an air pollution problem. Hydrocracking is a catalytic cracking process in the presence of hydrogen and has greater flexibility in adjusting operations to meet changing product demands. Wastewaters are high in sulfides and possibly in phenols and ammonia.

e. Hydrocarbon Rebuilding

Higher octane products for use in gasoline may be manufactured by two hydrocarbon rebuilding techniques: polymerization or alkylation. Wastewaters are high in sulfides, mercaptans, ammonia, suspended solids, and oils. Waste sulfuric acid is usually recovered.

f. Hydrocarbon Rearrangements

Isomerization and reforming are two process techniques for obtaining higher octane gasoline blending stock. Isomerization, a molecular rearrangement process, rather than a decomposition process, generates no major pollutant discharge. Reforming, a mild decomposition process, generates low volume discharges with small quantities of sulfides, ammonia, mercaptans, and oil present.

g. Solvent Refining

Various solvents are used to improve the quality of a particular feedstock component. The major pollutants are the solvents themselves, many of which can produce a high BOD. Under ideal conditions the solvents are continually recirculated. Actually, some solvent is always lost. Oil and solvent are major wastewater constituents.

h. Hydrotreating

Hydrotreating processes are used to purify and pretreat various feedstocks by reacting with hydrogen. Contaminants, including sulfur and nitrogen compounds, odor, color, and gum-forming materials are removed. The strength and quantity of wastewaters generated by hydrotreating depends upon the subprocess and feedstock used. Ammonia and sulfides are present. Phenols may also be present.

i. Grease Manufacturing

Grease is primarily a soap and lube oil mixture. A small amount of oil is lost to the wastewater system through leaks in the pumps. The largest waste loading occurs when the units are washed.

j. Asphalt Production

Asphalt feedstock is contacted with hot air at 203°C - 280°C to obtain a desirable asphalt product. Wastewaters contain high concentrations of oils which have high BOD. Small quantities of phenols may also be present.

k. Product Finishing

Drying and sweetening processes are used to remove sulfur compounds, water and other impurities from gasoline, kerosene, jet fuels, domestic heating oils and other middle distillate products. Spent caustic, large quantities of high BOD and COD sulfides and phenols are generated. Phenolic caustic streams are usually sold for recovery of phenolic materials.

Clay and acid treatment to remove color forming and other undesirable materials further refine lube oil stocks. Acid wastes high in dissolved and suspended solids, sulfates, sulfonates and stable oil emulsions are generated. Handling acid sludge can create additional problems. Some refineries neutralize the sludge and discharge it to the sewer, resulting in organic and inorganic pollution.

Blending various gasoline stocks and additives and packaging the products are relatively clean processes. The primary source of waste material is from tank car washing. These wash waters are high in emulsified oil. Tetra-ethyl lead, a gasoline additive, is highly toxic and may be washed into the sewer.

1. Auxiliary Activities

The manufacture of hydrogen for use in the hydrotreating and hydrocracking processes is a relatively clean one. A potential waste source is the desulfurization unit, if utilized, which contains oil, sulfur compounds and phenol.

Wastewaters are generated in the preparation of boiler feed water and in boiler blowdown.

The subcategories include various combinations of the processes previously discussed and are defined as follows:

Topping (A) - Includes all refineries which combine all processes except cracking and coking.

Cracking (B) - Includes refineries which contain topping, reforming and cracking operations. Also included are all first generation conventional refinery-associated products or intermediates, including benzene-toluene-xylene (BTX), alkanes, alkenes, alkynes, hydrogen and coke whose production is less than 15 percent of the refinery throughput.

Petrochemical (C) - Includes topping, cracking and petrochemical operations. Petrochemical operations include first generation conventional refinery-associated production or intermediates, including benzene-toluene-xylene (BTX), alkanes, alkenes, alkynes, hydrogen and coke whose production is more than 15% of the refinery throughput. It also includes second generation petrochemical production such as cumene, phthalic anhydride, alcohols, ketones, trimer and styrene.

Lube (D) - Includes topping, cracking and lube oil manufacturing operations. Lube oil feedstocks are recovered from the asphalt residues produced from the topping process. Lube oils are separated from asphalt by solvent extraction. This subcategory excludes formulating blended oils and additives.

Integrated (E) - Includes topping, cracking, lube oil and petrochemical operations.

4. Wastewater Characterization

The wastewaters generated by refining are diverse and complex, representing a full range of organic and inorganic materials. Some of these pollutants are biodegradable, some are removable by physical-chemical treatment. Tables 8-15-1 and 8-15-2 contain raw wastewater characteristics from this industry.

5. Control and Treatment Technology

In-Plant Control - There are two types of in-plant practices that reduce flow to the treatment plant:

A. Reuse practices involving the use of water from one process in another process. Examples of this are: using stripper bottoms for makeup to crude desalters; using blowdown from high pressure boilers as feed to low pressure boilers; and using treated effluent as makeup water wherever possible.

B. Recycle systems that use water more than once for the same purpose. Example of recycle system is: the use of steam condensate as boiler feedwater.

Another effective in-plant control is good housekeeping practices, including dry cleaning methods, to clean up oil spills, minimizing leaks, and treating segregated waste streams such as spent cleaning solutions.

Wastes generated by cleaning tanks and equipment during turnaround should be collected and gradually bled to the sewer after the necessary pretreatment steps.

Processes may be designed or modified to minimize waste load. Examples include:

A. Substitution of improved catalysts.

B. Replacement of barometric condensers with surface condensers or air fan coolers.

Table 8-15-1
Petroleum Refining Industry
Raw Wastewater Characteristics

Parameter (mg/1)	Topping A	Cracking B	Petrochemical C	Lube D	Integrated E
BOD	10-50	30-600*	50-800*	100-700*	100-800*
TSS	10-40	10-100	50-200	80-300	20-200
TDS	400-700	400-700	400-700	400-700	400-700
COD	50-150	150-400	300-600	400-700	300-600
Oil & Grease	10-50*	15-300*	20-250*	40-400*	20-500*
Phenols	0-200	0-100	.5-50	.1-25	.5-50
Nitrogen-Ammonia	.05-20	.5-200	4-300	1-120	1-250
Chromium	0-3*	0-6*	0-5*	0-2*	0-2*
Zinc	.04-1.84*	.04-1.84*	.04-1.84*	.04-1.84*	.04-1.84*
Cyanides	0-.2	0-.2	0-.2	0-.2	0-.2
Sulfides	0-5	0-400*	0-200*	0-40	0-60*
Phosphate	.1-10	.1-10	.1-10	.1-10	.1-10

Note: *See Appendix 5 for parameters which may be inhibitory to biological systems.

TABLE 8-15-2

PETROLEUM REFINING INDUSTRY
WASTEWATER CHARACTERISTICS BASED ON PRODUCTION

Parameter (kg/1000M^3)	Topping A	Cracking B	Petrochemical C	Lube D	Integrated E
Flow Range (gals per day)	67MM	93MM	110MM	118MM	235MM
Flow Type	C	C	C	C	C
BOD	3.5	73	172	218	198
TSS	11.7	18	49	72	58
COD	37.2	218	463	544	329
Oil & Grease	8.3	31.2	53	120	75
Phenols	.034	4	7.7	8.3	3.8
Nitrogen Ammonia	1.2	28.3	34.3	24	20.5
Chromium	.007	.25	.24	.046	.5
Sulfides	.055	.95	.86	.014	2

C Continuous

MM Million

C. Cooling towers enable recycling of cooling water many times, eliminating large volumes of once-through cooling water.

Many waste streams are routinely treated at the source, including stripping of sour waters, neutralization and oxidation of spent caustics, ballast water separation, and slop oil recovery. Sour water stripping removes 85-99% of the sulfides before it enters the sewer. Spent caustics are treated, and occasionally products are extracted and sold. Slop oil or separator skimmings are treated and reused.

Treatment Technology - End-of-pipe control technology relies heavily upon the use of biological treatment methods preceded by appropriate pretreatment to insure the proper conditions. Table 8-15-3 shows removal efficiencies of several wastewater treatment methods practiced by the industry.

Table 8-15-3
Petroleum Industry Wastewater Treatment Practices

Pollutant and Method	Removal Efficiency, %
BOD	
1. API Separator	5-40
2. Clarifier	30-60
3. Biological Treatment	40-99
4. Filter	40-70
5. Activated Carbon	70-98
COD	
1. API Separator	5-30
2. Clarifier	20-50
3. Biological Treatment	30-95
4. Filter	20-55
5. Activated Carbon	70-94
TSS	
1. API Separator	10-50
2. Clarifier	50-80
3. Biological Treatment	20-85
4. Filter	75-95
5. Activated Carbon	60-90
Oil	
1. API Separator	60-99
2. Clarifier	60-95
3. Biological Treatment	50-99
4. Filter	65-95
5. Activated Carbon	70-95
Phenol	
1. API Separator	0-50
2. Clarifier	0-50
3. Biological Treatment	60-99
4. Filter	5-20
5. Activated Carbon	90-100
Ammonia	
1. Biological Treatment	0-99
Sulfide	
1. Biological Treatment	70-100

1. General Industry Description

Steel mills may range from comparatively small plants to completely integrated steel complexes where great quantities of raw materials and resources are brought together to ultimately produce steel. Even the smallest of plants will generally represent a fair-sized industrial complex. Because of the wide product range, the operations vary significantly within each facility. Great quantities of water are used, both for processing and for cooling purposes. As a result, the iron and steel industry generates large volumes of wastewater. This industrial category includes Standard Industrial Classifications (SIC) 3312, 3313, 3315, 3316 and 3317.

2. Industrial Categorization

The iron and steel industry is composed of separate and distinct processes with enough variability in both product and waste characteristics to require categorization into more than one all-encompassing unit operation. Accordingly, the industry can be broadly subdivided into six major operational areas: coke making, burden preparation, iron making, steel making, forming and finishing and miscellaneous. The number and type of pollutant parameters of significant vary with the operation being conducted and the raw materials used. The waste volumes and waste loads also vary with the operation. For the purposes of raw waste characterization and delineation of pretreatment information, the industry is further subcategorized primarily along operational lines, with permutations where necessary, as shown in Table 8-16-1.

The code letters shown after the subcategories are used to identify them throughout this section. Process descriptions along with the products and important measurable effluents associated with each subcategory are provided below. The typical integrated steel mill in the industry will embody several of these subcategories and the discharges may be combined.

3. Process Descriptions

General

Five basic steps are involved in the production of steel in a modern integrated steel mill:

1. Coal is converted into coke by either the by-product process (A) or the beehive process (B). Coke fines generated in these processes are screened out before the coke can be used in the blast furnace.

2. Coke is combined with iron ore and limestone in a blast

TABLE 8-16-1

IRON AND STEEL MANUFACTURING

Main Category	Subcategory	Designation
1. Coke Making	By-Product Coke	(A)
	Beehive Coke	(B)
2. Burden Preparation	Sintering	(C)
3. Iron Making	Blast Furnace Iron	(D)
	Blast Furnace - Ferromanganese	(E)
4. Steel Making	Basic Oxygen Furnace (Semi-wet Air Pollution Control Methods)	(F)
	Basic Oxygen Furnace (Wet Air Pollution Control Methods)	(G)
	Open Hearth Furnace	(H)
	Electric Arc Furnace (Semi Air Pollution Control Methods)	(I)
	Electric Arc Furnace (Wet Air Pollution Control Methods)	(J)
	Vacuum Degassing	(K)
	Continuous Casting	(L)
5. Forming and Finishing	Hot Forming - Primary	(M)
	Hot Forming - Section	(N)
	Hot Forming - Flat	(O)
	Pipe and Tubes	(P)
	Pickling-Sulfuric Acid-Batch	(Q)
	Pickling-Hydrochloric Acid-Batch and Continuous	(R)
	Cold Rolling	(S)
	Hot Coatings - Galvanizing	(T)
	Hot Coatings - Terne	(U)
6. Miscellaneous	Misc. Runoffs - Storage Piles, Casting & Slagging	(V)
	Cooling Water Blowdown	(W)
	Utility Blowdown	(X)
	Maintenance Department Wastes	(Y)
	Central Treatment	(Z)

furnace to produce iron (D, E). Waste materials from the blast furnace include sizeable quantities of fine dust which are high in iron content.

3. Iron is converted into steel in either a basic oxygen furnace (F, G), an open hearth furnace (H), or an electric furnace (I, J). Further refinements include degassing (K) by subjecting the steel to a high vacuum. Steel is cast either by continuous casting (L) or in ingot molds. The slag generated in the steel making processes is transported and subjected to a slagging operation where the steel scrap is reclaimed and the slag crushed into a saleable product.

Waste materials from the steel making processes include sizeable quantities of fine dust which are high in iron content.

4. Iron bearing waste fines from the blast furnace and steel making processes are blended with limestone and coke fines in a sintering operation (C) for the purpose of agglomerating and recycling the fines back to the blast furnace. Processing of steel plant wastes (burden preparation) by pelletizing or by briquetting has also been proven on a pilot scale and several such plants are due on line in the near future.

5. The final step includes forming and finishing operations. Ingots are reduced to slabs or billets and ultimately to plates, shapes, strips, etc. through the forming operations. The steel finishing operations do little to alter the size or dimensions, but impart desirable surface or mechanical characteristics to the product.

A flow diagram of a typical steel mill is shown in Figure 8-16-1.

By-Product Coke (A)

Today the by-product process produces about 99 percent of all metallurgical coke. Bituminous coal is heated in ovens out of contact with air to drive off the volatile components. The residue in the ovens is coke; the volatile components are recovered and processed to produce tar, light oils, and other materials of potential value, including coke oven gas. Typical products from the carbonization of coal are gas, tar, ammonia, tar acids, hydrogen sulfide, light oil, coke and coke breeze.

The most significant liquid wastes are excess ammonia liquor, final cooling water overflow, light oil recovery wastes and indirect (Non-contact) cooling water. In addition, wastewaters may result from coke wharf drainage, quench water overflow and coal pile runoff. The final cooling water is a potential source of highly toxic cyanogen compounds. Light oil recovery wastes contain primarily phenol, cyanide, ammonia and oil. The effluent

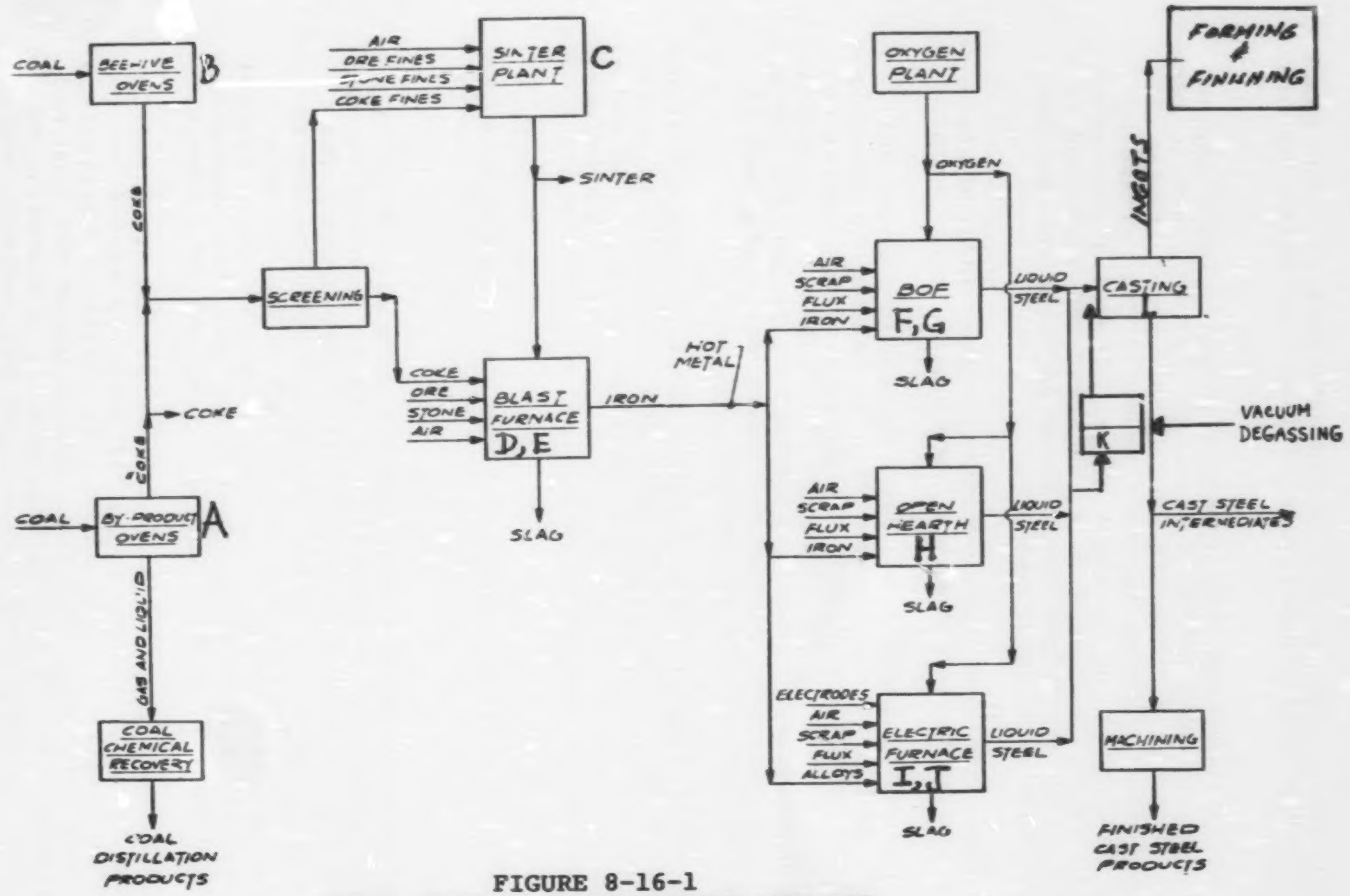

COAL
BEE-HIVE OVENS
B
COKE
COAL
BY-PRODUCT OVENS
A
COKE
COKE
GAS AND LIQUID
COAL CHEMICAL RECOVERY
COAL DISTILLATION PRODUCTS
SCREENING
AIR
ORE FINES
STONE FINES
COKE FINES
SINTER PLANT
C
SINTER
COKE
ORE
STONE
AIR
BLAST FURNACE
D, E
SLAG
IRON
HOT METAL
OXYGEN PLANT
OXYGEN
AIR
SCRAP
FLUX
IRON
BOF
F, G
SLAG
LIQUID STEEL
AIR
SCRAP
FLUX
IRON
OPEN HEARTH
H
SLAG
LIQUID STEEL
ELECTRODES
AIR
SCRAP
FLUX
ALLOYS
ELECTRIC FURNACE
I, J
SLAG
LIQUID STEEL
CASTING
INGOTS
FORMING & FINISHING
K
VACUUM DEGASSING
CAST STEEL INTERMEDIATES
MACHINING
FINISHED CAST STEEL PRODUCTS

FIGURE 8-16-1
STEEL PRODUCT MANUFACTURING PROCESS
FLOW DIAGRAM

from the quenching of coke, which is permitted to overflow to the sewer in some plants, contains trace amounts of cyanide, phenol and solids. Condensed steam and cooling water constitute the bulk of wastewaters discharged to the sewer in this subcategory.

Beehive Coke (B)

In this process for manufacturing coke, air is admitted to the coking chamber in controlled amounts for the purpose of burning the volatile products distilled from the coal to generate heat for further distillation. The beehive produces only coke and no other by-products are recovered. Water is used only for coke quenching.

A properly controlled beehive oven has very little water discharge. In some instances, an impoundment lagoon is provided to collect the overflow water and settle out coke fines. Discharges from this pond can contain phenol and cyanide, however recycle to extinction with zero discharge is currently practiced in some plants.

Sintering (C)

This plant has the primary function of agglomerating and recycling iron bearing waste fines back to the blast furnace. Sintering is achieved by blending the iron bearing components and limestone with coke fines which act as a fuel. The mixture is spread on a moving down draft grate and ignited. The down draft keeps the coke burning and the bed is brought to fusion temperature. The hot sinter is crushed, cooled, sized and formed into pellets and briquets.

Raw wastes from the sintering process emanate from the material handling dust control equipment and the dust and volatized oil in the process gases.

Most modern plants have fabric type dust collectors with no aqueous discharges. However, several plants utilize wet scrubbers and generate wastewaters which contain significant concentrations of suspended matter, oil, sulfide and fluoride. Usually aqueous discharges are associated with the pelletizing or briquetting operations. However, there is potential for wastewater from wet methods of dust control.

Blast Furnace - Iron (D)

Virtually all iron made in the world today is produced in blast furnaces which reduce iron ore to metallic iron. Iron ore, limestone and coke are charged into the furnace. Coke is burned to produce carbon monoxide which reacts with the ore to produce carbon dioxide and metallic iron. The major impurity of most iron ores and coke is silica which is removed by the limestone which combines with the silica to produce a molten mass called slag. As the molten iron leaves the blast furnace, the floating slag is skimmed off. The auxiliary operations associated with a blast furnace are raw material storage and handling, air compression and heating, gas cleaning, iron and slag handling and dust handling.

The blast furnace has two basic water uses - cooling water and gas washer water. Continuous circulation of cooling water is required to prevent the furnace walls from burning through. The principal wastewaters result from the gas cleaning operation. These wastewaters contain significant concentrations of cyanide, phenol, ammonia, sulfide and suspended solids. Phenol, cyanides, and ammonia originate in the coke and are particularly high if the coke has been quenched with wastewater or has not been completely coked. The suspended solids result from the fines in the burden being carried out in the gas.

Blast Furnace - Ferromanganese (E)

The blast furnace charge consists of iron and manganese ores, limestone and coke. The principal wastewaters are from the gas cleaning operation and contain significant concentrations of cyanide, phenol, ammonia, sulfide, manganese and suspended solids. Cyanide formation, due to the reaction of carbon from the coke with nitrogen from the blowing air, is particularly high at the higher temperatures of a ferromanganese furnace as compared to an iron furnace.

Basic Oxygen Furnace (F, G)

The raw materials for this steel making process are hot metal (iron), scrap steel, limestone, burnt lime, fluorspar, dolomite and iron ores. Alloying materials such as ferromanganese, ferrosilicon, etc., may be used to finish steel to the required specifications. The basic oxygen furnace uses pure oxygen to refine the hot metal (iron) and all other metallics into steel by oxidizing and removing the elements present such as silicon, phosphorus, manganese, and carbon. Oxides such as silicon dioxide, manganese oxide, phosphorus pentoxide, and iron oxide are fluidized in the slag which floats on the metal surface while oxides of carbon are emitted as gas. The wastes from this process are heat, airborne fluxes, slag, carbon monoxide and dioxide gases and oxides of iron.

Basic oxygen furnaces are always equipped with gas cleaning systems for containing and cooling huge volumes of hot gases (1,650°C) and submicron fumes released. Water is used to quench the offgases. Two main process types are used for gas cleaning: precipitators and venturi scrubbers. For venturi scrubbers, the gases are quenched and saturated to 80°C, whereas for the precipitators the gases are cooled to about 250°C. If venturi scrubbers are used, the majority of airborne contaminants are mixed with water and discharged as effluents. Generally, water clarification equipment is provided for the treatment of this effluent.

In addition to the fume collection cooling water system, the basic oxygen furnace has three main water systems:

1. Oxygen Lance Cooling Water System

2. Furnace Trunnion Ring Cooling Water System

3. Hood Cooling Water System

The oxygen lance cooling water system is either a "once-through" or a "closed recirculation" system. The furnace trunnion ring cooling is generally a "once-through" system with a discharge differential temperature increase of about 20°C. The hood cooling water system may be a recirculating type using induced draft cooling towers with chemical treatment. If water of good quality and sufficient quantity is available, "once-through" cooling systems are sometimes employed.

Open Hearth Furnace (H)

Open hearth furnaces can utilize an all-scrap steel charge but generally a 50-50 charge of hot metal and steel scrap is used. The furnace front wall is provided with water cooled lined doors for charging raw materials into the furnace. A plugged tap hole at the base of the wall opposite to the doors is provided to drain the finished molten steel into ladles. Fuel in the form of oil, coke oven gas, natural gas, pitch, creosote, tar, etc., is burned at one end of the furnace to provide heat for melting of scrap and other process requirements.

The open hearth process has two plant water systems: The furnace cooling water system and the fume collection water system. Furnace cooling is a once-through system with heated aqueous discharges of 17-22°C differential temperature. The fume collection systems are either wet high energy venturi scrubbers or dry precipitators.

The aqueous discharges from precipitators are zero except for any waste heat boiler blowdown. The discharges from the scrubbers are wastewaters from the primary quenchers with concentrations of fluoride, nitrates, suspended solids and zinc.

Electric Arc Furnace (I, J)

The electric arc furnace steel making process produces high quality and alloy steel in refractory lined cylindrical furnaces utilizing a cold steel scrap charge and fluxes. Sometimes, a lower grade of steel produced in the basic oxygen furnace or the open hearth furnace is alloyed in the electric arc furnace.

The heat for melting the scrap charge, fluxes, etc., is furnished by passing an electric current through the scrap or steel bath by means of three consumable cylindrical carbon electrodes inserted through the furnace roof. The heat cycle generally consists of charging, meltdown, molten metal period, oxidizing, refining and tapping. Pure oxygen is sometimes lanced across the bath to speed up the oxidation cycle. The waste products from the process are smoke, slag, carbon monoxide and dioxide gases and oxides of iron emitted as submicron fume. Zinc oxides from galvanized scrap may be released depending upon the type and quality of scrap.

The electric arc furnace has two main plant water systems: The furnace cooling water system and the fume collection cooling water system. The former is generally a "once-through" system but may be a "closed recirculation" system; the latter can range from completely dry to semiwet to wet systems using precipitators, bag houses, or high energy, venturi scrubbers. Semi-wet systems are generally "once-through", with a temperature differential of 17-22°C in cooling waters. However, recycle to extinction with no discharge is also practiced. The wet high energy venturi scrubber fume collection systems produce aqueous discharges similar to the basic oxygen wastewater.

Vacuum Degassing (K)

In the vacuum degassing process, steel is further refined by subjecting the ladle to a high vacuum in an enclosed refractory lined chamber. Steam jet ejectors with barometric condensers are employed to draw the vacuum. Certain alloys are added which may be drawn into the gas stream. The system is purged with nitrogen to eliminate residual carbon monoxide.

The wastewater from this process contains suspended solids, zinc, manganese, lead and nitrates.

Continuous Casting (L)

In the continuous casting process, billets, blooms, slabs and other shapes are cast directly from the teeming hot metal, thus eliminating the ingots, molds, soaking pits and stripping facilities. Three water systems serve the casting machine: Mold cooling, machine cooling, and spraying. Mold and machine cooling are performed in closed recycle streams. Wastewaters result from washing scale from the steel surface with spray water and contain significant quantities of suspended matter and oil.

Hot Forming - Primary (M)

Hot forming defines the initial stages in forming useful products from steel ingots by hot-rolling. The basic operation of a primary mill is the gradual cross-sectional reduction of a hot steel ingot into blooms and slabs between the surfaces of two rotating steel rollers, and the progression of the ingot through the space between the rolls. The hot steel ingots are transferred to the primary mills for rolling from soaking pit furnaces which consist of square, rectangular, or circular, fuel-fired refractory lined pits. After delivery to the mill, the ingot is generally weighed on a scale and sent to the rolling mill stand. During the rolling operation, cooling water is sprayed extensively over the table and mill stand rolls. This water is discharged to trenches beneath the rolling mill equipment. It is also necessary to use high pressure (2000 psi) descaling water for spray over the hot ingot to flush away iron oxide scales that form on the hot ingot. The blooms are passed through hot-scarfing machines after leaving the bloom shares to remove defects from the surface of the bloom. Fume control is required and water sprays carry the iron oxide wastes through a trench under the mills to a collection system.

Hot Forming - Section (N)

Blooms from the primary mill are conveyed directly to the billet mill without reheating. The billets are further processed to produce material with small sections, such as tube rounds, bar and rod, and special products. Modern billet mills utilize continuous mills which have alternate horizontal and vertical stands. The continuous mill consists of a series of roll stands, arranged one after the other so that the piece to be rolled enters the first stand and travels through the mill, taking one pass in each stand and emerging from the last set as a finished product. Descaling water and cooling water are sprayed at the stands and rolls with the discharge going to the trenches under the mills. After the billet mills, the product is cut to the desired finish piece length. The billets are cooled on cooling beds and pushed into cradles, from which they can be loaded into cars for shipment or transferred for further processing. Smaller quantities of mill scale are generally generated in the hot forming-section subcategory than in the primary rolling operation but the particle size may be smaller and more difficult to settle out.

Hot Forming - Flat (O)

This subcategory embodies the operations associated with plate mills, hot strip mills, and skelp mills. The basic operation of a plate mill is the reduction of a heated slab to the weight and dimensional limitations of plates. This is accomplished by heating the slabs, descaling, rolling to plates, leveling or flattening, cooling, and shearing to the desired size. Descaling is completed on the delivery side of the mill as the slab is passed through top and bottom high pressure hydraulic sprays operating at 1,000 psi to 1,500 psi. About 4 percent of the spray water evaporates and the balance is discharged through a trench under the mills to an iron oxide and water collection system. During the rolling operation, cooling water is sprayed externally over the table and mill stand rolls.

The basic operation of a hot strip mill is the reduction of slab to flat strip steel in thicknesses of 0.04 in. to 1.25 in., widths of 24 in. to 96 in., and lengths of up to 2,000 ft. Principal water uses include descaling water sprays and cooling water.

Skelp is a hot-rolled strip used to make butt-weld pipe or tube. Skelp is rolled from a heated bloom and has a width which corresponds to the circumference of the pipe and a gauge which corresponds to the thickness of the wall. Descaling water, cooling water, and water-soluble oil sprays accompany the rolling operation.

Pipe and Tubes (P)

Typical steel tubular products are standard pipe, conduit pipe, line pipe, pressure pipe, structural pipe, oil-country tubular goods, pressure tubes, mechanical tubes, and stainless steel pipe and tubes. Butt-welded pipe or tube is made from a hot-rolled strip. By heating this skelp to the welding temperature and drawing it through a die or roll pass, it is bent into cylindrical shape and its edges pressed firmly together into a butt-weld, thus forming a pipe. Seamless tubular products are made either by "piercing" or by "cupping." In the former process, a solid round bar or billet is heated, pierced and then shaped to the desired diameter and wall thickness. In cupping, a circular sheet or plate is forced by successive operations through several pairs of conical dies until the plate takes the form of a tube or cylinder with one end closed. Electric-resistance-welded tubing (ERW) is made from strip sheet or plate. The steps in the manufacture of ERW are: forming, welding, sizing, cutting, and finishing. Plates are converted into pipes by the electric-weld process by shearing, planing, crimping, bending, welding, expanding, and finishing.

Significant pollutants in the wastewaters resulting from this subcategory include suspended solids and oil and grease. Wastewaters originate from contact cooling waters such as roll spray cooling waters and cooling bed or spray quench waters. Suspended solids can be traced to the scale which is flushed off the pipe surface by the roll cooling spray waters. Oil and grease originate in the hydraulic and lubricating systems.

Pickling-Sulfuric Acid-Batch (Q) and Pickling-Hydrochloric Acid-Batch and Continuous (R)

Pickling is the chemical removal of surface oxides (scale) from metal by immersion in a heated solution. Carbon steel pickling is almost universally accomplished by using either surfuric acid (Q) or hydrochloric acid (R). The acid conditions vary with the type of material to be pickled. In addition, bath temperature, use of inhibitors, and source of agitation are also varied depending on the material to be pickled. Pickling is done by either continuous strip or batch type operations. Continuous strip pickling lines use horizontal pickling tanks. Large, open tanks of a wide range of sizes are used for batch type pickling, principally for rod coils, bars, billets, sheet, strip, wire, and tubing. Pickling is also applicable to forgings, castings, structural parts, and other items.

In continuous pickling, fresh acid solution is added to the last tank section and cascades through the tanks to an overflow located in the first section. Acid solution flow is opposite to the direction of the strip travel. In batch type pickling, the tanks are generally rubber lined and brick sheathed and hold a large volume of heated acid solution. Sulfuric acid is most often used for this purpose. After a certain iron buildup due to iron scale removal, the batch acid solution is considered spent and umped. The pickling is followed by the rinse operation which may vary from a one-step dunk to more sophisticated multi-stage rinsing. The primary purpose of rinsing is to remove the contaminants prior to the next sequence in the process. The first rinse removes the bulk of contaminants. The next rinse section can be either dunk rinse or spray. The water from this section is used to replenish the first-stage rinse section. The last stage uses clean, fresh water as the washing medium to insure a clean product. It may be possible to use the contaminated rinse water as input water to the fume scrubber, prior to its final disposition as pickle recycling system makeup water.

Most continuous strip pickling lines employ the traditional approach to rinsing: flooding the strip with hundreds of gallons of waters per minute to wash away the few gallons of acid that may be dragged out of the pickling tanks. Multi-stage spray rinsing systems can easily be incorporated into new continuous strip pickling lines, and they can be installed in existing lines in place of the present rinsing sections.

Acid fumes are prevalent in the pickling process and must be removed in order to provide a good working environment. To remove the acid from the exhaust stream, washing or filtration methods may be applied. In scrubbers, the acid droplets are contacted with water, trapped, and then flushed away. Acid mist filters use specially designed synthetic fibers in a filter box which is installed in the discharge end of an exhaust system. This system releases water vapor to the atmosphere while it collects the acid droplets and returns them to the pickle tank. The acid mist filter controls air pollution and simultaneously recovers acid for reuse.

Wastewaters in the pickling-sulfuric acid-batch subcategory (Q) originate in either of two forms: as spent solutions of concentrated waste pickle liquor containing iron and sulfuric acid; or as dilute solutions resulting from dunk or spray rinsing of pickled product. The significant pollutants in the pickling-hydrochloric acid-batch and continuous subcategory (R) include suspended solids, total iron, ferrous iron, dissolved iron and pH.

Cold Rolling (S)

In cold rolling, cooled hot strip mill product is passed through a pair of rolls for the purpose of reducing its thickness, producing a smooth dense surface, and developing controlled mechanical properties in the metal. Cold reduction is a special form of cold rolling in which the thickness of the starting material is reduced by relatively large amounts in each pass through the rolls. In tempering, the thickness of the material is reduced only a few percent to impart the desired mechanical properties and surface characteristics to the final product. During rolling, the steel becomes quite hard and unsuitable for most uses. As a result, the strip must undergo an annealing (heating) operation to return its ductility and to effect other changes in mechanical properties suitable for its intended use. This is done in either a batch or continuous annealing operation.

Wastewaters from this subcategory originate when water, oil, oil-in-water emulsions, oil-water-detergent solutions or combinations of any of these rolling solutions, used for cooling or lubricating the rolls, are dumped. Suspended solids and oil and grease are the important pollutants.

Hot Coatings-Galvanizing (T) and Hot Coatings-Terne (U)

Coating is the application of a layer of one substance to completely cover another. In the iron and steel industry, coatings are applied for a variety of reasons. Most often, a relatively thin layer of a metallic element such as zinc, chromium or aluminum is applied to carbon steel, imparting such desirable qualities as resistance to corrosion, safety from contamination, or decorative appearance. In addition to metallic coatings, non-metals, simple and complex organic compounds, miscellaneous inorganic materials such as vitreous enamel, and metallic powders in silicate paints are also used as coating materials. All methods of applying coatings to steel surfaces require careful surface preparation which is the primary and most important step in the process. Commonly used for this purpose are alkaline or solvent cleaning for grease removal, acid pickling for removing scale or rust, and physical desurfacing using abrasives or brushes. Following surface preparation, metallic coatings may be applied by one of the following processes: hot dip process, electroplating, metal spraying, metal cementation, fuse welding, metal cladding.

Hot dipped coating using steel baths of molten metal is practiced as a batch-dip operation. In hot coating-galvanizing (T), the coated products are withdrawn from the bath, subjected to drying with a warm air blast, or chemically treated with ammonium chloride, sulfur dioxide, chromate or phosphate solutions to produce special galvanized finishes and surface characteristics. Terne is an inexpensive, corrosion-resistant, hot-dipped coating (U) consisting of lead and tin. A major portion of all terne coated materials is used in the automobile industry to manufacture gasoline tanks, automotive mufflers, oil pans, air cleaners, and radiator parts. Batch and continuous terne coating operations both exist, though the continuous process is by far the larger portion of the market.

Wastewaters in the hot coating-galvanizing (T) subcategory result from cleaning operations, chemical treatment, and rinses applied to the product before or after coating as well as batch discharges from the various solutions and baths. Suspended solids, oil and grease, zinc, chromium and pH are the principal pollutants. Wastewaters in the hot coating-terne subcategory originate from similar sources and contain suspended solids, oil and grease, lead, tin, and pH.

Subcategories V-Z

There are no iron and steel manufacturing processes associated with subcategories V-Z, as this miscellaneous category covers ancillary operations within a mill. Wastewaters resulting from these operations are highly variable in both quality and quantity.

4. Wastewater Characteristics

The characteristics of process wastewaters are shown in Table 8-16-2. In addition to the pollutants listed in the table, thermal discharges may also be generated.

The steel industry operates throughout the year and generates wastewaters over a 24-hour day. Wastewater volume and characteristics are subject to hourly variations. The process wastewaters are generally treated on site before disposal.

Wastewaters are subject to wide variations in flow within individual subcategories. This is largely due to the diversity in the plant cooling water systems and the fume collection and cooling systems.

The BOD in the wastewaters of the steel industry is mostly due to the coke manufacturing processes. However, cold rolling and blast furnace wastewaters will also contribute some BOD. Coking process waters are generally amenable to biological treatment only if they comprise less than 25 percent of the total wastewater.

TABLE 8-16-2

IRON AND STEEL MANUFACTURING
RAW WASTEWATER CHARACTERISTICS

Parameter	By-Product Coke	Beehive Coke	Sintering	Blast Furnace Fe	Blast Furnace Fe - Mn	BOF (Semiwet)	BOF (Wet)	Open Hearth Furnace	Electric Arc Furnace (Semiwet)	Electric Arc Furnace (Wet)	Vacuum Degassing	Continuous Casting
	A	B	C	D	E	F	G	H	I	J	K	L
Flow Range[1] (1/kkg)	171/19182	513/2040	434/1420	8050/ 22500	32,200	542/3040	1080/ 4250	2290/ 2530	1.01/406	751/1250	813/3750	6172/17100
Flow Type	A	B	C	C	C	C	C	C	C	C	C	C
BOD_5[2]	12-1550*	0-3										
SS	23-421	29-722	4340- 19500	307- 1720	5,000	321-396	180- 5330	388- 3880	77-863	2160- 42800	23-70	7.-74.
pH												
Ammonia	39-7330*	0-0.33		1.-12.	141							
Oil and Grease	2.-240*		457-504									20.5-22.0
Cyanide#	7.7-110*			0-1	23.6*							
Phenol	6.1-910	0-.01			0.13							
Sulfide	4.2-629*		64.-188*	0-40								
Fluoride			0-.6	0-2		0-2.	0-11	16-20		10-15		
Manganese					833*						5-13*	
Nitrate								20.-33.*			3.-25*	
Zinc								2-880*	0-13*	405*- 5637*	2*-8*	
Lead											.4*-1*	

NOTE:
1. 1/kkg of product produced (lower limit/upper limit)
2. All concentrations represent net raw wastes and are in mg/l except as noted.
B. Batch Process
C. Continuous Process

* See Appendix 5 for parameters which may be inhibitory to biological systems.
# With acclimation higher levels can be tolerated.

TABLE 8-16-2(continued)

IRON AND STEEL MANUFACTURING
RAW WASTEWATER CHARACTERISTICS

Parameter	Hot Forming Primary	Hot Forming Section	Hot Forming Flat	Pipe and Tubes	Pickling Sulfuric Acid-Batch	Pickling Hydrochl. Acid-Batch & Contin.	Cold Rolling	Hot Coatings Galvanizing	Hot Coatings Terne	Misc. Runoffs	Cooling Water Blowdown	Utility Blowdown	Maint. Dept. Wastes	Central Treatment
	M	N	O	P	Q	R	S	T	U	V	W	y	Y	Z
Flow Range[1] (l/kkg)	330/6210	7980/ 138,200	18,900/ 35,200	2150/ 53,300	23/1630	12/4720	73/2135	5,146	2150/ 9150	Variable	Variable	Variable	Variable	Variable
Flow Type													B	
BOD_5 (mg/l)[2]										15				
SS	4-91	12-125	6-57	27-103	21-159		90-900	98	8-48	412	Present	Present	Present	
pH										7.6	6-9	6-9		
Ammonia														
Oil and Grease	2-14	0-14	2-10	0-61*			54*- 41,140*	19	73*				Present	
Cyanide#										3.2*				
Phenol														
Sulfide														
Fluoride														
Manganese														
Nitrate														
Zinc								14.5*			Present			
Lead									0.20					
Total Iron					42*- 7,900*	134*- 117,000*								
Sulfates					105- 26,000*					592-890				
Chlorides						3- 200,000*								

NOTE: 1. l/kkg of product produced (lower limit/upper limit)
2. All concentrations represent net raw wastes and are in mg/l except as noted.
B. Batch Process

* See Appendix 5 for parameters which may be inhibitory to biological systems.
# With acclimation higher levels can be tolerated.

5. Control and Treatment Technology

In-Plant Control

Significant in-plant control of both waste quantity and quality is possible for some important subcategories of the iron and steel manufacturing industry. In by-product coke making (A) wastewaters are generated by the coking process and there also is usually a wastewater discharge from the coke quenching operation. The wastewaters from the by-product coke making operation (A) are highly contaminated and require intensive treatment. Wastewater from coke quenching can be reduced by dry coke quenching or simply by routing the wharf drains to the quench tower as make-up water and not allowing any overflow from the quench tower. Zero liquid discharge from modern coke plants can be achieved by evaporation of all liquid to dryness since the pollutants are mostly volatile except approximately 1% dissolved solids (chlorides, etc.), but this would be accompanied by potential air pollution problems. The effluent gases from less than optimum incineration of the wastewater can be expected to contain high concentrations of nitrogen oxides, sulfur oxides, and some particulate matter.

Liquid discharges from the blast furnace subcategories (D,E) can be significantly reduced by recycling the gas cleaning and cooling water. Modern blast furnace practice has shown that this water could be put through settling chambers to remove the suspended solids and over a cooling tower to remove the heat.

The liquid discharge exclusive of non-contact cooling water for all of the steel making processes - basic oxygen (F,G), open hearth (H), and electric furnace (I,J) - results from the gas cleaning operations. Although the technology for dry gas cleaning lags behind the requirements for gas cleanliness, reductions in flow or pollutant loads from these subcategories are still feasible by the use of recycle systems and closeup of semi-wet systems.

In the hot forming-primary subcategory (M), an important control measure relating to all contact cooling, descaling and scarfing wastewaters is the periodic cleaning of scale pits to remove buildup of mill scale which otherwise will wash through. The same measure is also applicable to the hot-forming-section (N) and hot forming-flat (O) subcategories. Complete recycle with no blowdown, makeup as needed, and cooling tower or pond cooling for hot mills will result in zero discharge of wastewaters from the pipe and tubes subcategory (P). While this is practiced in some mills it may not be accomplished under all circumstances. In the pickling-sulfuric acid-batch subcategory (Q), on site recovery of acid from concentrates, rinses, and fume scrubber effluents, and the recovery of iron as ferrous hepthahydrate crystals can eliminate aqueous discharges. However, high initial capital costs are involved which may be eventually balanced by recovery of usable products. In hydrochloric acid pickling (R), reuse of all acid rinse waters to make up fresh batches or pickle liquor is possible. In cold rolling (S), recycle of rolling solutions and use of treated wastewaters on cold rolling lines can significantly reduce discharges. In hot coatings (T, U), control of wastewater volumes through counter-current rinses and by use of fume hood scrubber recycle systems, and special attention to maintenance of equipment designed to reduce loss of solution are effective means for reducing discharge loads.

Treatment Technology

The iron and steel manufacturing industry utilizes a broad range of treatment technology in control of its effluents. Table 8-16-3 presents a brief summary of the treatment practices employed in each subcategory, and the pollutant removals achievable with each treatment process.

TABLE 8-16-3

IRON AND STEEL MANUFACTURING
WASTEWATER TREATMENT PRACTICES
REMOVAL EFFICIENCIES, PERCENT

Pollutant and Method	By-Product Coke A	Beehive Coke B	Sintering C	Blast Furnace Fe D	Blast Furnace Fe-Mn E	BOF (Semi-wet) F	BOF (wet) G	Open Hearth Furnace H	Electric Arc Furnace (Semi-wet) I	Electric Arc Furnace (wet) J	Vacuum Degassing K	Continuous Casting L
Suspended Solids												
1. Chemical Coagulation & Thickening			99		99	91	99	98	100	99		
2. Sedimentation & Filtration	74			97							97	97
BOD												
1. Activated Sludge & Clarification	98											
2. Settling	48	80										
Ammonia												
1. Solvent Recovery, Ammonia Stripping & Settling	93											
2. Settling		40		25								
Phenol												
1. Activated sludge or Solvent Extraction	99			90								
Nitrate												
1. Bio-Denitrification								91			94	
Zinc												
1. Chemical Coagulation and Thickening								70				
2. Settling and Filtration											99	
Fluoride												
1. Coagulation and Sedimentation								42	60	10		

TABLE 8-16-3 (continued)

IRON AND STEEL MANUFACTURING
WASTEWATER TREATMENT PRACTICES
REMOVAL EFFICIENCIES, PERCENT

Pollutant and Method	Hot Forming Primary	Hot Forming Section	Hot Forming Flat	Pipe and Tubes	Pickling Sulfuric Acid-Batch	Pickling Hydrochl. Acid-Batch & Contin.	Cold Rolling	Hot Coatings Galvanizing	Hot Coatings Terne	Fugitive Runoffs	Cooling Water Blowdown	Utility Blowdown	Maint. Dept. Wastes	Central Treatment
	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z
Suspended Solids														
1. Clarification, Chemical Treatment & Filtration	99	99	99	99			99							
2. Sedimentation				80				80						
Oil & Grease														
1. Primary and Secondary Clarification, including Skimming	85	85	85				80		85					
2. Air Flotation, Chemical Treatment, & Clarification							90							

1. General Industry Description

The Nonferrous Metals Industry concerns itself with the smelting and refining of nonferrous metals including aluminum, copper, lead and zinc. This description does not include the mining of the materials or manufacturing of final products based on these metals.

In general, wastes from this industry are low in BOD and COD, but may be high in dissolved and suspended solids.

This industry includes Standard Industrial Classifications (SIC) 2819, 333 and 334.

2. Industrial Categorization

Subcategory	Designation
Bauxite Refining	A
Primary Aluminum Smelting	B
Secondary Aluminum Smelting	C
Primary Copper Smelting	D
Primary Copper Refining	E
Secondary Copper	F
Primary Lead	G
Primary Zinc	H

3. Process Description

Bauxite Refining (A)

Bauxite is the principal ore of aluminum and the only one used commercially in the United States. Bauxite is composed of hydrated aluminum oxide and impurities such as iron oxide, aluminum silicate, titanium dioxide, quartz, and compounds of phosphorus and vanadium. The process for refining bauxite is the Bayer process, in which the impure alumina is dissolved in a hot strong alkali solution to form sodium aluminate. The solution is diluted and cooled whereby sodium aluminate hydrolyzes and precipitates and is then filtered out of solution, and calcined to alumina. Figure 8-17-1 is a flow diagram for the Bayer Process.

The major waste stream is "Red Mud", which contains the impurities rejected from the bauxite. The red mud consists of 17-20% solids. Other waste streams include air scrubber effluents, barometric condenser effluents, cooling water, chemical cleaning wastes, and spills and leaks.

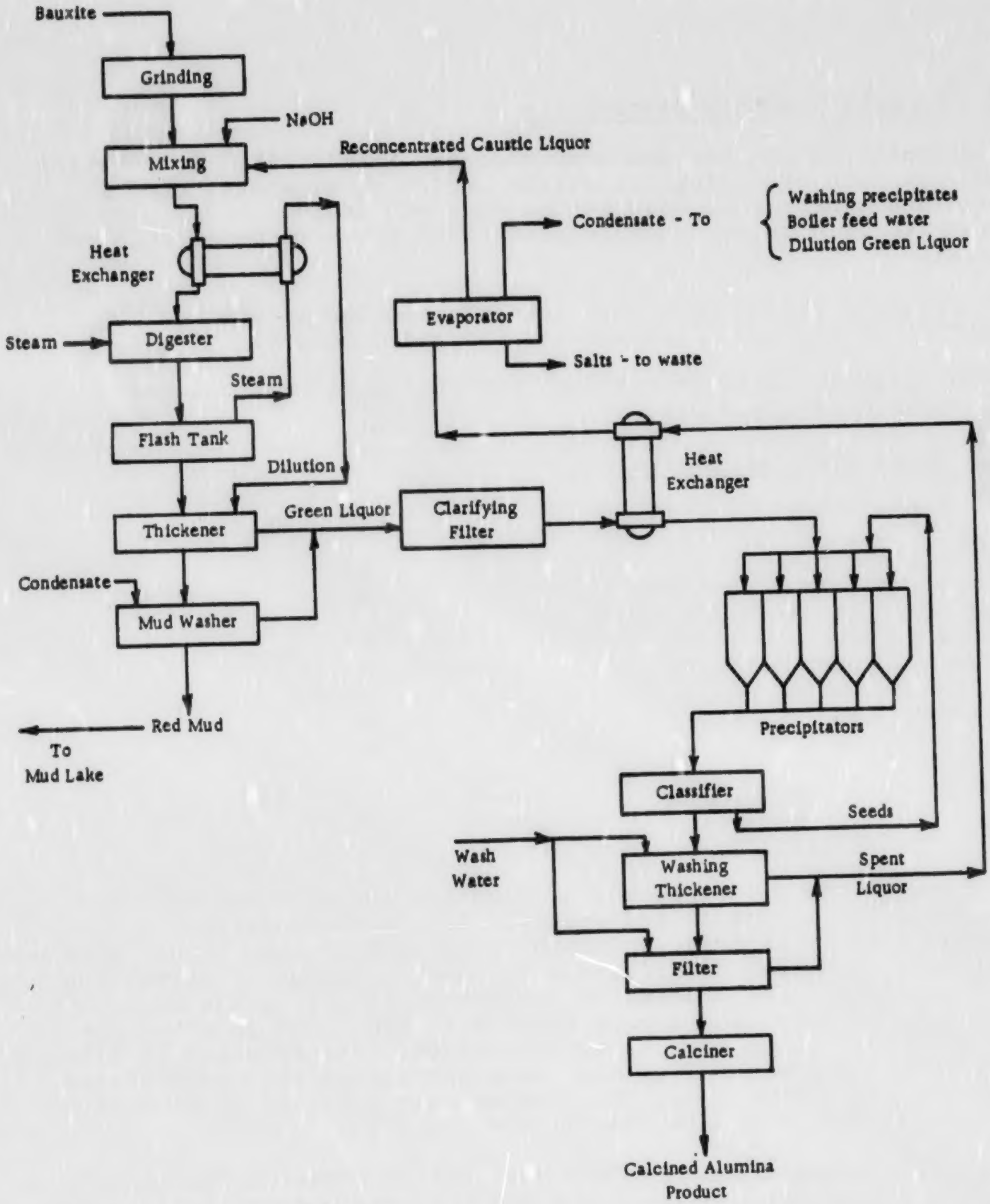

Bauxite
Grinding
NaOH
Mixing
Reconcentrated Caustic Liquor
Heat Exchanger
Condensate - To
Washing precipitates
Boiler feed water
Dilution Green Liquor
Evaporator
Steam
Digester
Salts - to waste
Steam
Flash Tank
Heat Exchanger
Dilution
Thickener
Green Liquor
Clarifying Filter
Condensate
Mud Washer
Red Mud
To Mud Lake
Precipitators
Classifier
Seeds
Wash Water
Washing Thickener
Spent Liquor
Filter
Calciner
Calcined Alumina Product

FIGURE 8-17-1
BAUXITE REFINING(A)
GENERALIZED DIAGRAM OF THE BAYER PROCESS
NONFERROUS METALS INDUSTRY

Primary Aluminum Smelting (B)

The primary aluminum process is defined as the reduction of purified aluminum oxide (alumina) to produce aluminum metal by the Hall-Heroult process and electrolytic process. A process flow diagram is shown in Figure 8-17-2. The reduction of alumina to produce aluminum metal is carried out in electrolytic cells, or pots, connected in series to form a potline. The facility containing a number of potlines is referred to as the potroom. The electrolysis takes place in a molten bath composed of cryolite, a double fluoride of sodium and aluminum. Alumina is added to the bath periodically. As electrolysis proceeds, aluminum is deposited at the cathode (as a liquid) and oxygen is evolved at the carbon anode. The oxygen reacts with the carbon anode to produce carbon monoxide and carbon dioxide. The anode is consumed and must be replaced periodically. The liquid aluminum produced is tapped periodically, and the metal is cast in a separate casthouse facility. The molten metal is degassed before casting by bubbling chlorine or a mixed gas through the melt. The chlorine degassing procedure produces a fume which must be scrubbed for air pollution control, producing a waste stream.

The continuous evolution of gases at the anode described above yields a large volume of fume. This gas stream also has to be scrubbed, producing a waste stream.

The cathode of the aluminum reduction cell is a carbon liner on which the pool of aluminum rests. During service the cathode becomes impregnated with bath materials and must be replaced. Water contacting spent electrodes has a significant fluoride content due to leaching action, and may represent a source of contamination.

Other waste streams from this process are cooling waters used in casting, rectifiers and fabrication, and boiler blowdown.

Secondary Aluminum Smelting (C)

The secondary aluminum smelting subcategory is defined as that segment of the industry which recovers, processes and remelts aluminum scrap to produce metallic aluminum or an aluminum alloy. Figure 8-17-3 is a flow diagram for this process. Aluminum scrap is prepared for smelting and refining in a variety of ways. Some plants employ wet processing techniques to wash the feed, and carry away fluxing salts and chemicals, thus generating a wastewater.

The scrap metal is then charged to the furnace where flux, and alloying agents are added. The molten metal is mixed in the furnace to insure uniform composition of the material. Magnesium impurities are removed in the furnace by a process called "demagging" which is the addition of chlorinating agents or aluminum fluoride to produce magnesium compounds that can be scraped off the top of the melt. This operation produces fumes, which if treated with wet scrubbers, produces a waste stream.

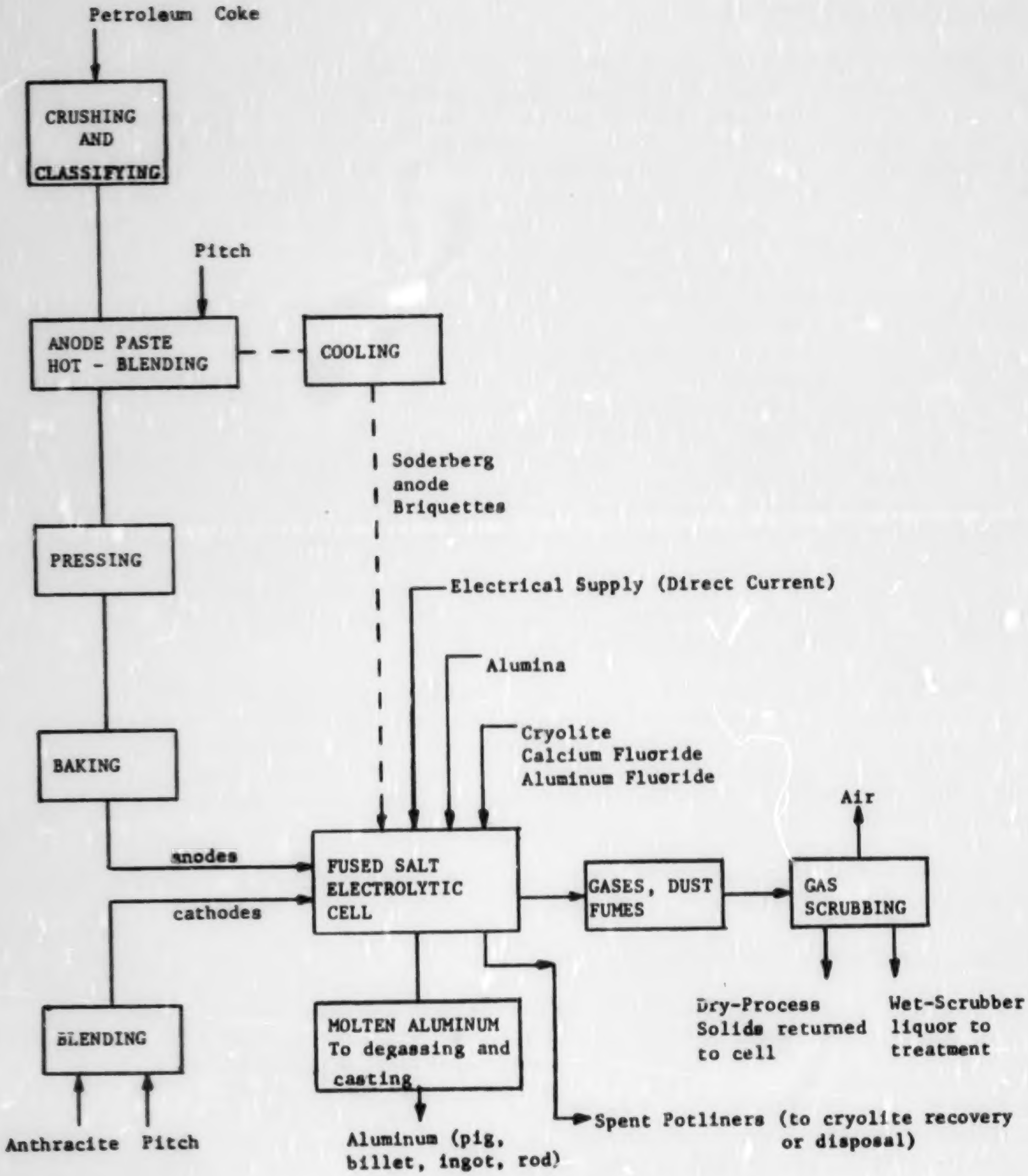

Petroleum Coke
CRUSHING AND CLASSIFYING
Pitch
ANODE PASTE HOT - BLENDING
COOLING
Soderberg anode Briquettes
PRESSING
Electrical Supply (Direct Current)
Alumina
Cryolite
Calcium Fluoride
Aluminum Fluoride
BAKING
Air
anodes
cathodes
FUSED SALT ELECTROLYTIC CELL
GASES, DUST FUMES
GAS SCRUBBING
Dry-Process Solids returned to cell
Wet-Scrubber liquor to treatment
BLENDING
MOLTEN ALUMINUM To degassing and casting
Spent Potliners (to cryolite recovery or disposal)
Anthracite
Pitch
Aluminum (pig, billet, ingot, rod)

FIGURE 8-17-2
PRIMARY ALUMINUM SMELTING(B)
PROCESS DIAGRAM FOR THE ELECTROLYTIC PRODUCTION OF ALUMINUM
NONFERROUS METALS INDUSTRY

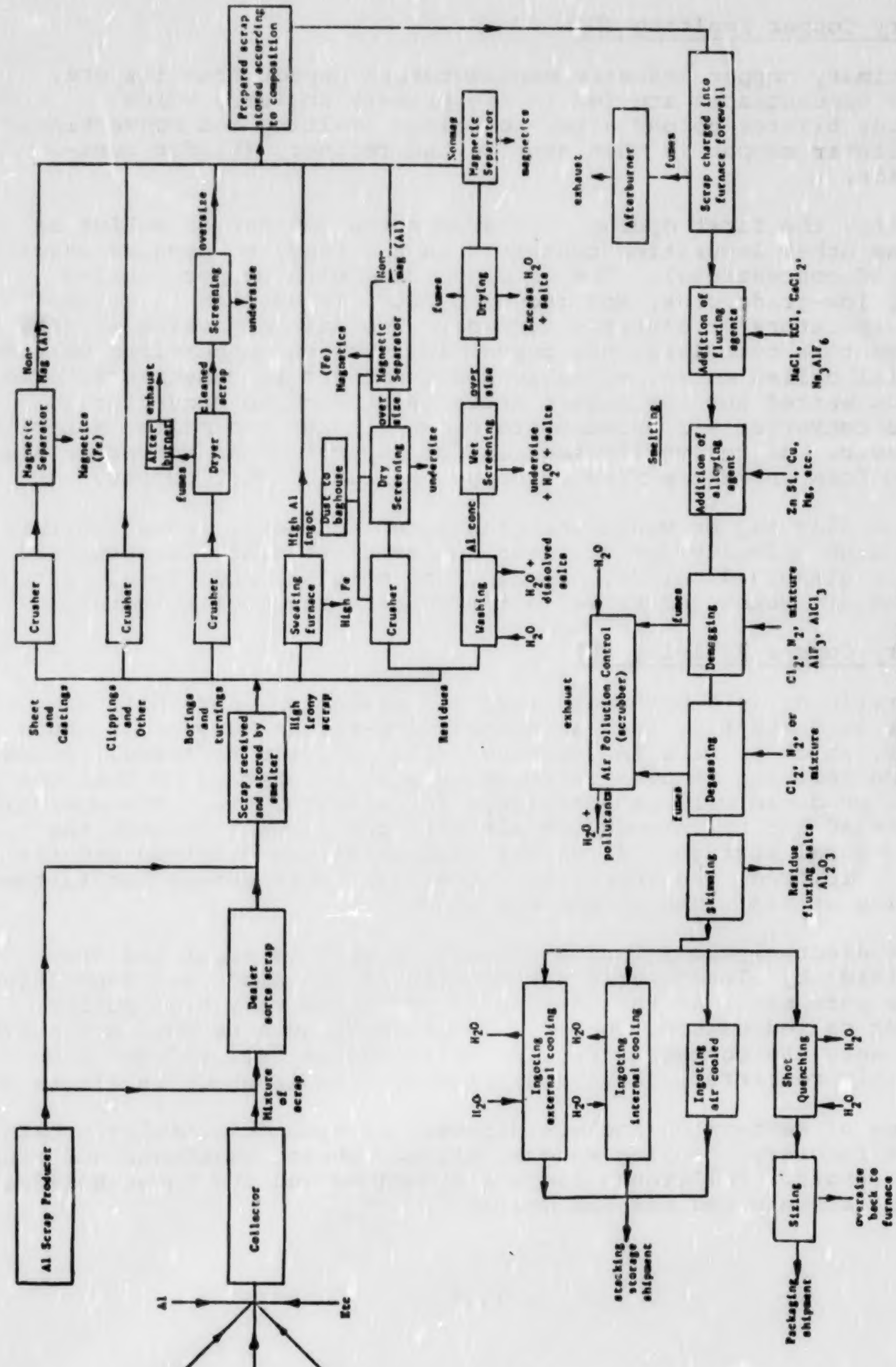

Al Scrap Producer
Collector
Cu
Zn
Fe
Al
Etc
Mixture of scrap
Dealer sorts scrap
Scrap received and stored by smelter
Sheet and Castings
Clippings and Other
Borings and turnings
High irony scrap
Residues
Crusher
Crusher
Crusher
Crusher
Magnetic Separator
Non-Mag (Al)
Magnetics (Fe)
fumes
After burner
exhaust
Dryer
Cleaned scrap
Screening
oversize
undersize
Sweating furnace
High Fe
High Al Ingot
Dust to baghouse
Dry Screening
undersize
over size
Magnetic Separator
(Fe) Magnetics
Non-mag (Al)
Washing
H2O
H2O + dissolved salts
H2O
Al conc
Wet Screening
undersize + H2O + salts
over size
Drying
fumes
Excess H2O + salts
Nonmag
Magnetic Separator
magnetics
Prepared scrap stored according to composition
Scrap charged into furnace forewell
fumes
Afterburner
exhaust
Addition of fluxing agents
NaCl, KCl, CaCl2, Na3AlF6
Addition of alloying agent
Zn Si, Cu, Mg, etc.
Smelting
Demagging
Cl2, N2, mixture AlF3, AlCl3
fumes
Degassing
Cl2, N2, or mixture
fumes
Air Pollution Control (scrubber)
exhaust
H2O + pollutants
Skimming
Residue fluxing salts Al2O3
Ingoting external cooling
H2O
H2O
Ingoting internal cooling
H2O
H2O
Ingoting air cooled
Shot Quenching
H2O
H2O
Sizing
oversize back to furnace
stacking storage shipment
Packaging shipment

FIGURE 8-17-3
SECONDARY ALUMINUM PROCESS (C)
NONFERROUS METALS INDUSTRY

Primary Copper Smelting (D)

The primary copper industry manufacturers copper from its ore. Copper concentrates are fed to the primary smelter, which produces blister copper after roasting, smelting and converting. The blister copper is then sent to the refinery (E) for purification.

Roasting, the first operation, reduces the content of sulfur as well as other impurities contained in the feed, to produce calcine (roasted concentrate). The calcine along with copper-bearing scrap, low-grade ores, and recycled slag, is smelted in either a reverberatory or electric furnace. The main objective of this treatment is to collect the copper in a molten copper-iron-sulfide material called matte, suitable for treatment in converters. The slag is wasted and the molten matte is charged to converters. In the converter air streams are blown through the molten material to oxidize and remove iron and sulfur impurities as converter slag and to form an impure form of copper called blister copper.

Furnace slag may be wasted or granulated and sold. Some smelters use a high velocity jet of water to granulate slag. Wastewaters contain dissolved solids, arsenic, and metals. Additional waste streams are generated by wet air scrubbers and cooling water.

Primary Copper Refining (E)

Fire refining is a pyro-metallurgical operation where blister copper is further refined as either fire-refined copper or anode copper, which is used in subsequent electrolytic refining. Anode furnace refining removes large amounts of impurities so that the anodes produced will be acceptable for electrolysis. The operation is carried out by introducing air into the furnace beneath the molten metal surface. After the impurities are oxidized and the slag is removed, the copper is either cast into anodes for further refining or cast into shapes and sold.

In the electrolytic refining process, copper is separated from impurities by electrolytic dissolution at the amode and deposition as the pure metal at the cathode to produce a very high purity product called cathode copper. By-products such as gold and silver which were the contaminants, are collected as "slimes" and subsequently recovered. A process flow diagram is shown in Figure 8-17-4.

Sources of wastewater include disposal of spent electrolytic baths, slimes recovery, cooling waters, air scrubbers, washdowns and stormwater runoff. Pollutants include dissolved and suspended solids, metals, arsenic and oil and grease.

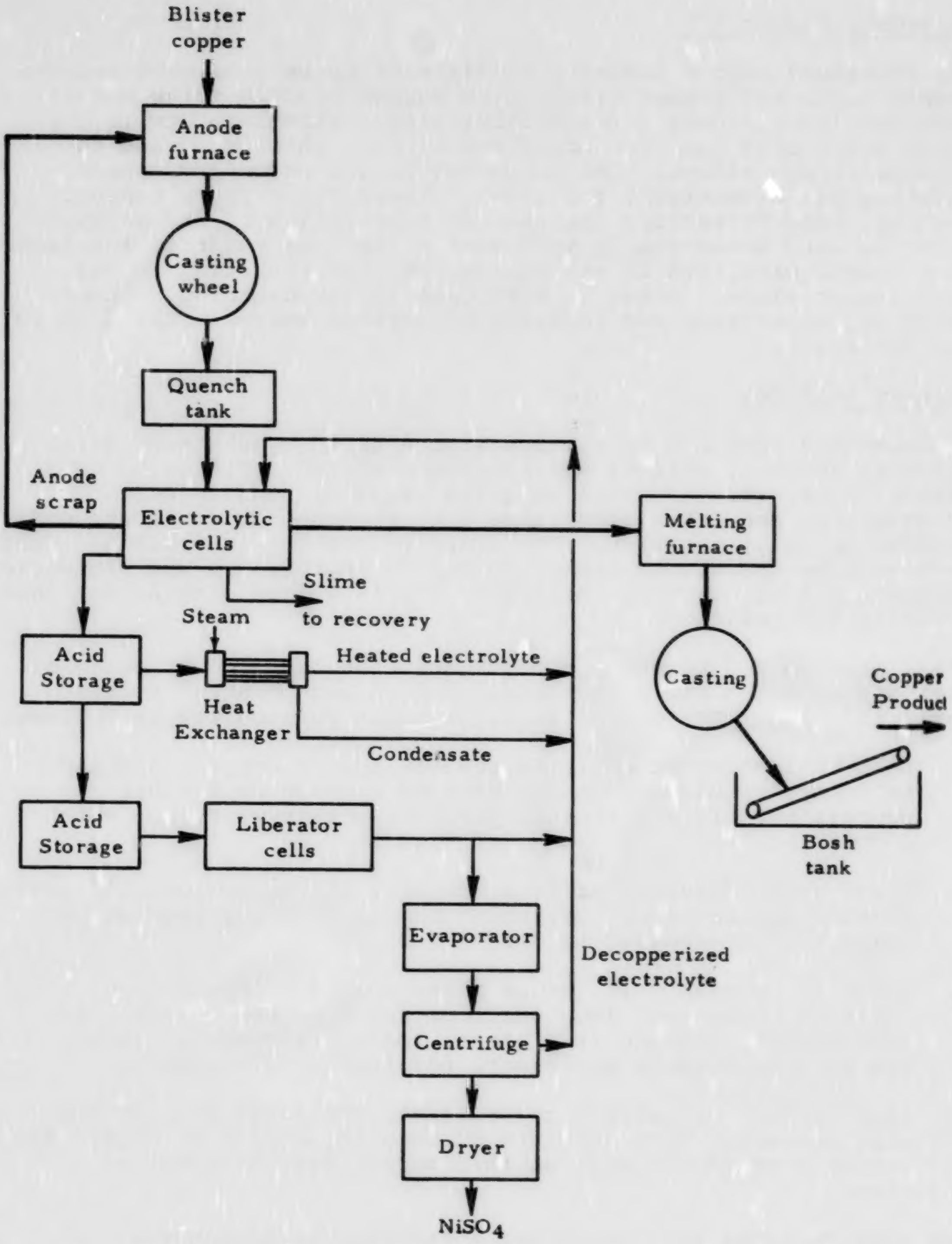

Blister copper
Anode furnace
Casting wheel
Quench tank
Anode scrap
Electrolytic cells
Melting furnace
Slime to recovery
Steam
Acid Storage
Heated electrolyte
Casting
Copper Produc
Heat Exchanger
Condensate
Acid Storage
Liberator cells
Bosh tank
Evaporator
Decopperized electrolyte
Centrifuge
Dryer
NiSO4

FIGURE 8-17-4
ELECTROLYTIC COPPER REFINING (E)
NONFERROUS METALS INDUSTRY

Secondary Copper (F)

The secondary copper industry consists of operations that recover copper metal and copper alloys from copper-bearing scrap metal and smelting residues (e.g. spills, slags, skimming, etc.). Scrap metal also includes brass and bronze, which are used to produce copper alloys. The processes in the secondary copper industry are essentially the same as those for primary copper. However, some variations are used in preparation of the scrap. Water is used occasionally in hammer mills used to strip insulation from copper wire, and in wet milling and concentrating copper from copper slags. Water is also used in air cleaning systems. Smelting, converting and refining operations were discussed in (D) and (E) above.

Primary Lead (G)

Concentrated lead ore is blended with a flux (a substance which promotes fusion), pelletized and then sintered. Sintering on a sintering machine (a traveling grate furnace) removes sulfur by oxidation and other impurities such as arsenic, antimony, and cadmium by volatilization. The sintered product is crushed. Dusts generated by the sizing operation may be captured by wet scrubbers generating a wastewater. Figure 8-17-5 is a flow diagram for lead smelting and refining.

The sinter is fed to the blast furnace whereby a combination of heat and reducing gases it separates into two phases: molten metal and slag. The products of the blast furnace are as follows:

a. Lead bullion which contains quantitites of copper, arsenic, antimony, or bismuth which must be removed by further processing. It may contain precious metals which are worth recovering.

b. Slag, which consists of iron, calcium and magnesium silicates, arsenic and antimony. Granulating the slag may generate a wastewater (discussed in D).

c. Matte and speiss - The matte phase consists of a liquid layer of copper and iron sulfides and precious metals. If considerable arsenic is present, speiss is formed. These are sent to outside processors for further treatment.

The lead bullion is subject to drossing, the first step of the refining process, which consists of removing copper by adjusting the temperature of the melt so that copper separates out of solution.

The next refining step is called softening, which removes antimony. Softening is accomplished in a furnace or by treatment of bullion with a sodium hydroxide sodium nitrate mixture.

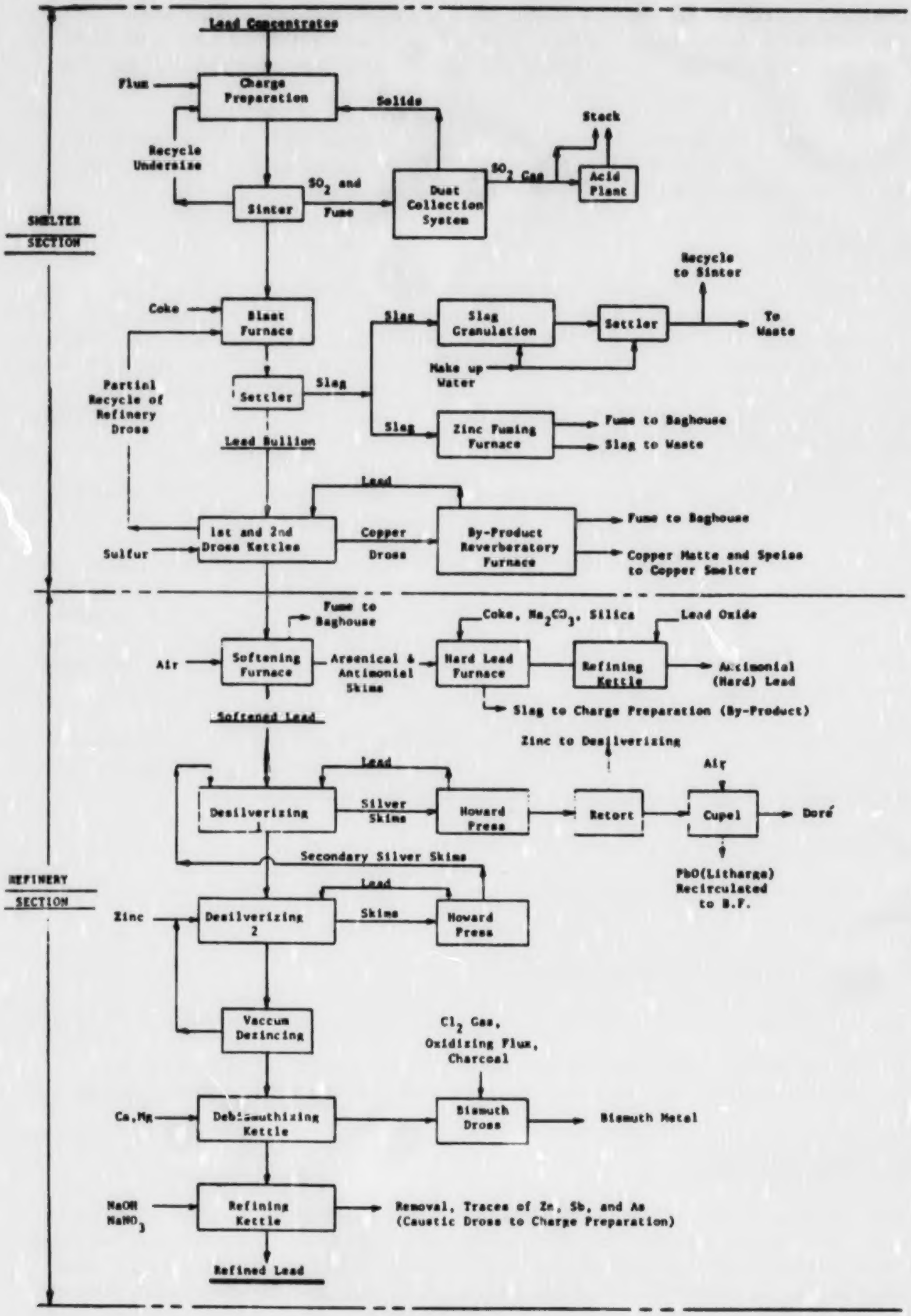

Lead Concentrates
Flux
Charge Preparation
Solids
Stack
Recycle Undersize
Sinter
SO2 and Fume
Dust Collection System
SO2 Gas
Acid Plant
SMELTER SECTION
Recycle to Sinter
Coke
Blast Furnace
Slag
Slag Granulation
Settler
To Waste
Make up Water
Partial Recycle of Refinery Dross
Settler
Slag
Slag
Zinc Fuming Furnace
Fume to Baghouse
Slag to Waste
Lead Bullion
Lead
1st and 2nd Dross Kettles
Copper Dross
By-Product Reverberatory Furnace
Fume to Baghouse
Sulfur
Copper Matte and Speiss to Copper Smelter
Fume to Baghouse
Coke, Na2CO3, Silica
Lead Oxide
Air
Softening Furnace
Arsenical & Antimonial Skims
Hard Lead Furnace
Refining Kettle
Antimonial (Hard) Lead
Slag to Charge Preparation (By-Product)
Softened Lead
Zinc to Desilverizing
Lead
Air
Desilverizing 1
Silver Skims
Howard Press
Retort
Cupel
Doré
Secondary Silver Skims
PbO(Litharge) Recirculated to B.F.
REFINERY SECTION
Lead
Zinc
Desilverizing 2
Skims
Howard Press
Vaccum Dezincing
Cl2 Gas, Oxidizing Flux, Charcoal
Ca,Mg
Debismuthizing Kettle
Bismuth Dross
Bismuth Metal
NaOH
NaNO3
Refining Kettle
Removal, Traces of Zn, Sb, and As
(Caustic Dross to Charge Preparation)
Refined Lead

FIGURE 8-17-5
GENERALIZED FLOW SHEET OF A LEAD
SMELTER AND REFINERY (G)
NONFERROUS METALS INDUSTRY

The softened lead bullion is then fire refined to separate gold, silver and bismuth. The final refining operation consists of adding caustic soda to remove calcium and magnesium from the metal.

Wastewaters are produced from noncontact cooling, gas scrubbing, and direct cooling and cleaning water from process operations. Pollutants include dissolved solids and metals.

Primary Zinc (H)

There are two types of zinc producing processes used in this country: the pyrolytic process and the electrolytic process shown in Figures 8-17-6 and 8-17-7. Both processes begin with the roasting operation in order to remove sulfur and other impurities and take place in a furnace. In the pyrolytic process, the operations include: sintering, briquetting, reduction, refining, and cadmium recovery.

In the electrolytic process the operations include: reduction and cadmium recovery.

Sintering and briquetting are preparation steps which produce an acceptable feed to the furnace. Refining consists of removing impurities such as lead and iron. Since there is a large quantity of cadmium in zinc ore, it is recovered as a by product from the air pollution control equipment (bag houses) in the roasting and sintering operations.

Wastewaters from zinc production come from non-contact cooling water, wet air scrubbers, contact cooling waters, spent process liquors, boiler blowdowns, and spills and leaks.

4. Wastewater Characterization

Tables 8-17-1 and 8-17-2 contain wastewater characteristics for this industry.

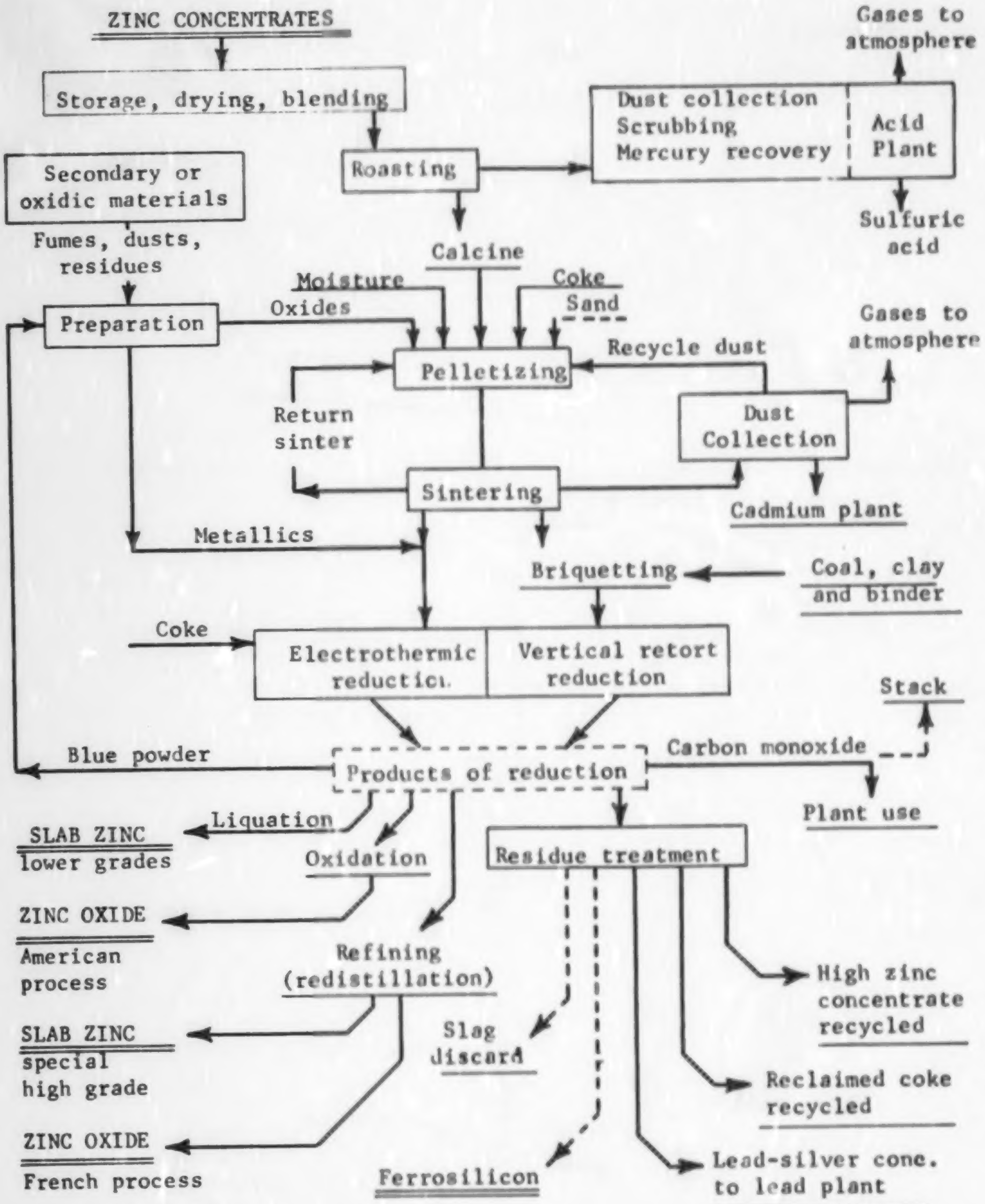
5. Control and Treatment Technology

In-Plant Control

Wet scrubbing water may be eliminated by substituting dry air cleaning techniques, or may be minimized by recycling scrubber water.

Bauxite Refining (A)

The major waste from this subcategory is "red mud," and the only treatment for this waste is impoundment. Due to the large volume of red mud produced compared to the other wastes generated, the most practical treatment of the other wastes is to impound them with the red mud.



ZINC CONCENTRATES
Storage, drying, blending
Roasting
Dust collection
Scrubbing
Mercury recovery
Acid Plant
Gases to atmosphere
Sulfuric acid
Secondary or oxidic materials
Fumes, dusts, residues
Calcine
Moisture
Coke
Sand
Oxides
Preparation
Pelletizing
Recycle dust
Gases to atmosphere
Return sinter
Dust Collection
Sintering
Cadmium plant
Metallics
Briquetting
Coal, clay and binder
Coke
Electrothermic reduction
Vertical retort reduction
Stack
Blue powder
Products of reduction
Carbon monoxide
Plant use
Liquation
SLAB ZINC lower grades
Oxidation
Residue treatment
ZINC OXIDE American process
Refining (redistillation)
High zinc concentrate recycled
Slag discard
SLAB ZINC special high grade
Reclaimed coke recycled
ZINC OXIDE French process
Ferrosilicon
Lead-silver conc. to lead plant

FIGURE 8-17-6
PYROLYTIC ZINC PROCESSING(H)
GENERALIZED FLOWSHEETS OF PYROLYTIC ZINC PLANTS
NONFERROUS METALS INDUSTRY

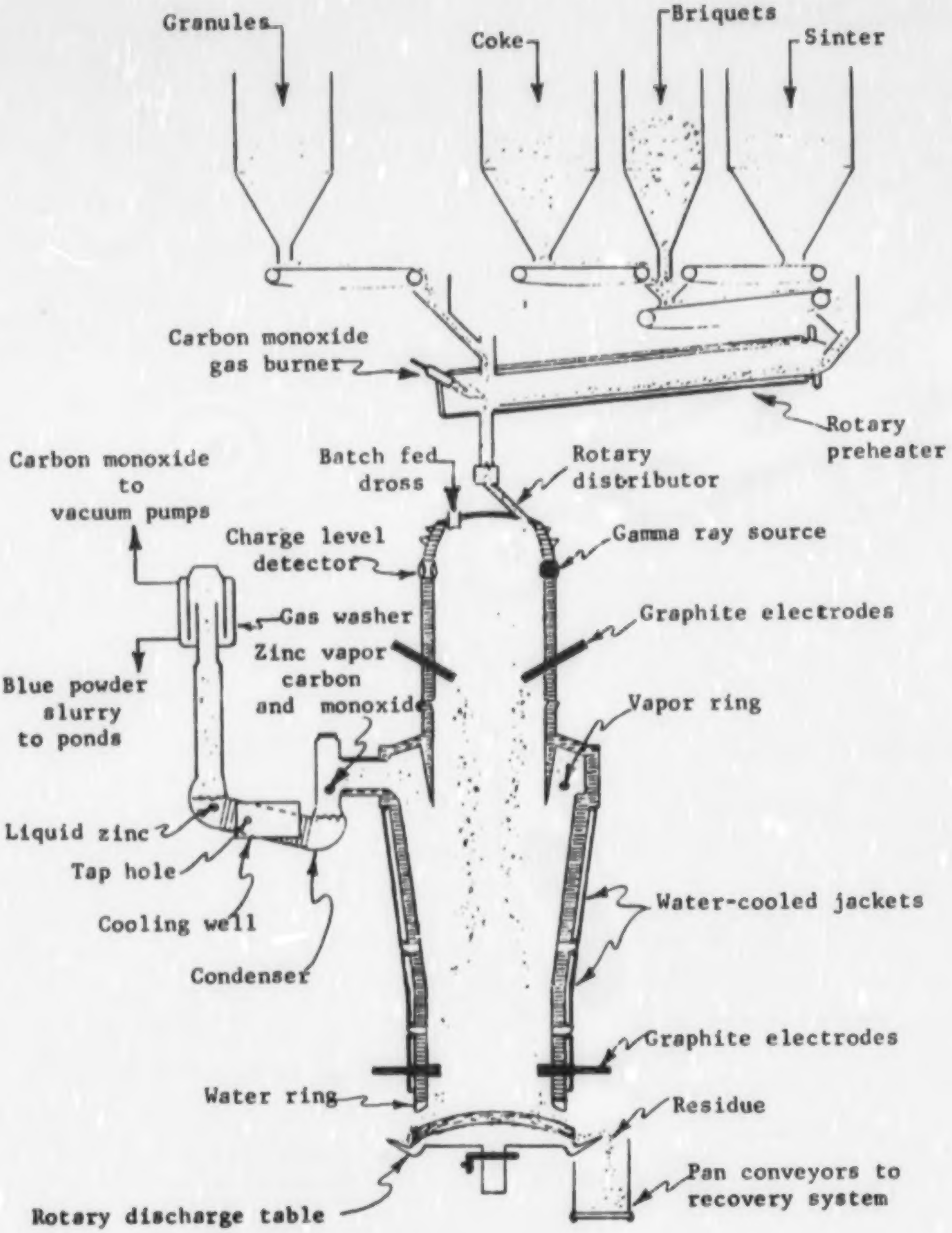

Granules
Coke
Briquets
Sinter
Carbon monoxide gas burner
Rotary preheater
Carbon monoxide to vacuum pumps
Batch fed dross
Rotary distributor
Charge level detector
Gamma ray source
Gas washer
Graphite electrodes
Zinc vapor carbon and monoxide
Blue powder slurry to ponds
Vapor ring
Liquid zinc
Tap hole
Cooling well
Condenser
Water-cooled jackets
Graphite electrodes
Water ring
Residue
Pan conveyors to recovery system
Rotary discharge table

FIGURE 8-17-7
ELECTROLYTIC ZINC PROCESS(H)
NONFERROUS METALS INDUSTRY

TABLE 8-17-1
NONFERROUS METALS
RAW WASTEWATER CHARACTERISTICS

WASTE PARAMETERS(mg/l)	SUBCATEGORY						
	Bauxite Refining A	Primary Aluminum Smelting B	Secondary Aluminum Smelting C	Primary Cooper Smelting and Refining D, E	Secondary Copper F	Lead G	Zinc H
Flow, GPD	Red Mud Discharge 17-20% Solids		(Wet Air Scrubbing Only)	145M - 7M			0 - 1MM
TSS		10 - 800	200 - 500	25 - 500	10 - 140	35 - 500	25 - 250
TDS		20 - 1M*	2M* - 10M*	160 - 15M*	150 - 2M*	500 - 1M*	450 - 4.5M*
COD		15 - 150	120 - 540	20 - 450	10 - 40	8 - 200	
Copper			0.2 - 1.3*	0.01 - 25*	0.2 - 8*	0.1 - 0.2	0.01-0.3
Zinc			1*- 3.6*	0 - 2.6*	0.3 - 18*	0.5*- 10*	5*-250*
Fluoride		15 - 1.4M*	0.2-0.7	No Data	0 - 35	No Data	
Aluminum		0 - 70	6 - 500	0 - 10	Nil	No Data	Nil
Oil and Grease		10 - 20	6 - 14	0 - 50*	2 - 8	No Data	0 - 10
Lead						0.3-0.5	0.02 - 1.3*

Notes: M = 1,000
MM = 1,000,000
*See Appendix 5 for parameters which may be inhibitory to biological systems

TABLE 8-17-2
NONFERROUS METALS INDUSTRY
RAW WASTEWATER CHARACTERISTICS
BASED ON PRODUCTION

WASTE PARAMETER	SUBCATEGORY						
	Bauxite Refining A	Primary Aluminum Smelting B	Secondary Aluminum Smelting C*	Primary Copper, Smelting and Refining D, E	Secondary Copper F	Lead G	Zinc H
Flow, (L/KKG)				1.2M - 57M			
Flow Type	Red Mud Discharge 1/3-2 KKG/KKG		Wet Air Scrubbing Only*				
TSS (Kg/KKG)		0.5-16	22-85	0.2 - 1	0.1 - 10	0.35-2	0.5-2.5
TDS (Kg/KKG)		1-24	200-2M	0.2 - 7	0.02 - 35	1-2	0.2-40
COD (Kg/KKG)		0.6-12	12-100	0.2 - 0.5	0.002 - 2	0-0.7	0.1-0.6
Copper (Kg/KKG)			0.02-0.2	0 - 0.04	0 - 0.6	0	Nil
Zinc (Kg/kkg)			0.1-0.6	0 - 0.1	0 - 0.5	0.004-0.04	0.1-0.5
Fluoride (Kg/KKG)		0.3-15		No Data	0 -0.03	No Data	No Data
Aluminum (Kg/KKG)		0.03-1.3	0.6-51	0 - 0.03	Nil	No Data	No Data
Oil & Grease (Kg/KKG)		0.04-0.5	0.4-0.6	0.003 - 0.03	0.05 -8	No Data	0.04-0.2
Lead (Kg/KKG)						Nil	0-0.02

Notes: M = 1,000
MM = 1,000,000
* Units gram/kilogram of magnesium removed for all values in this column.

Primary Aluminum Smelting (B)

Control of wastewaters consists essentially of using dry scrubbers or recycling the water used in wet scrubbers.

Secondary Aluminum Smelting (C)

Direct metal cooling wastewater can be eliminated by the use of air cooling, or by recirculating with the use of cooling towers. There are processes available that eliminate the fume (the Derham process and the Alcoa process) thus eliminating wet scrubbers.

Primary Copper Smelting (D) and Primary Copper Refining (E)

The wastewater from slag handling can be recycled back to the system, with the slag being used for landfill. Impoundment of other wastewaters and recirculation of the water from the pond is practiced at most mills, thus eliminating water discharges.

Secondary Copper (F)

Contact cooling water can be clarified, cooled, and then recirculated, eliminating a waste stream. Alternatives to this include the use of air for cooling, and the use of non-contact cooling water (cooling through the molds instead of putting the cooling water directly on the metal). Slag handling water can be impounded and then recirculated.

Primary Lead (G) and Primary Zinc (H)

Impoundment and recycle (previously described) apply to these two subcategories.

Treatment Technology

Much of the wastewater produced by this industry can be greatly reduced or totally eliminated by in-plant control measures. However, those streams that are only partly eliminated or not controllable with in-plant measures can be treated by the following systems:

1) neutralization (pH control)
2) clarification, with oil and grease removal
3) cryolite or lime precipitation
4) adsorption on activated alumina or activated carbon
5) reverse osmosis

1. General Industry Description

The phosphate manufacturing industry includes the production of elemental phosphorus, phosphorus derived chemicals, and other non-fertilizer phosphate chemicals. Phosphorus derived chemicals are phosphoric acid (dry process), phosphorus pentoxide, phosphorus pentasulfide, phosphorus trichloride, phosphorus oxychloride, sodium tripolyphosphate, and calcium phosphates. The non-fertilizer phosphate segment of the industry includes defluorinated phosphate rock, defluorinated phosphoric acid, and sodium phosphate salts. Mined phosphate rock and wet process phosphoric acid are the basic raw materials for this industry.

Wastewater volumes resulting from the production of phosphorus are several orders of magnitude greater than the wastewaters generated in any of the other product categories. Elemental phosphorus is an important wastewater contaminant common to all segments of the phosphate manufacturing industry if the phossy water (water containing colloidal phosphorus) is not recycled to the phosphorus production facility.

The phosphate manufacturing industry is designated by Standard Industrial Classification (SIC) 2819.

2. Industrial Categorization

The phosphate manufacturing industry is broadly subdivided into two main categories: phosphorus derived chemicals, and other non-fertilizer phosphate chemicals. For the purposes of raw waste characterization and delineation of pretreatment information, the industry is further subdivided into 6 subcategories, as follows:

Main Category	Subcategory	Designation
1. Phosphorus Derived Chemicals	Phosphorus Production	(A)
	Phosphorus Consuming	(B)
	Phosphate	(C)
2. Other Non-Fertilizer Phosphate Chemicals	Defluorinated Phosphate Rock	(D)
	Defluorinated Phosphoric Acid	(E)
	Sodium Phosphates	(F)

3. Process Description

General

An overall product manufacturing flow diagram for the industry is depicted in Figure 8-18-1. Manufacture of phosphorus derived chemicals is almost entirely based on the production of elemental phosphorus from mined phosphate rock. Ferrophosphorus, widely used in the metallurgical industries, is a direct by-product of the phosphorus production process. Over 87 percent of elemental phosphorus is used to manufacture high-grade phosphoric acid by the furnace or dry process as opposed to the wet process which converts phophate rock directly into low-grade phosphoric acid. The remainder of the elemental phosphorus is either marketed directly or converted into chemicals such as phosphorus pentoxide, phosphorus pentasulfide, phosphorus trichloride, and phosphorus oxychloride. The furnace-grade phosphoric acid is marketed directly, largely to the food industry and to the fertilizer industry. Phosphoric acid is also used to manufacture sodium tripolyphosphate which is used in detergents and for water treatment, and calcium phosphate which is used in foods and animal feeds.

Defluorinated phosphate rock is utilized as an animal feed ingredient. Defluorinated phosphoric acid is mainly used in the production of animal food stuffs and liquid fertilizers. Sodium phosphates produced from wet process acid as the raw material are used as intermediates in the production of cleaning compounds.

Phosphorus Production (A) - Phosphorus is manufactured by the reduction of mined phosphate rock by coke in an electric furnace, with silica used as a flux. Slag,ferrophosphorus (from iron in the phosphate rock), and carbon monoxide are reaction by-products. The standard process, as shown in Figure 8-18-2, consists of three basic parts: phosphate rock preparation, smelting in electric furnace, and recovery of phosphorus. Phosphate rock ores are first blended so that the furnace feed is of uniform composition. The blended rock is pretreated by heat drying, by agglomerating the particles, and by heat treatment. Sizing or agglomeration is accomplished by pelletizing, briquetting, or flaking, and pre-formed agglomerates are then calcined in a rotary kiln. The burden of treated rock, coke and sand is charged to the furnace by incrementally adding weighed quantities of each material to a common belt conveyor. The furnace itself has a carbon crucible, carbon-lined steel sidewalls, and a concrete roof. The furnace is extensively water-cooled. Slag and ferrophosphorus are tapped periodically. The hot furnace gases, consisting of 90%

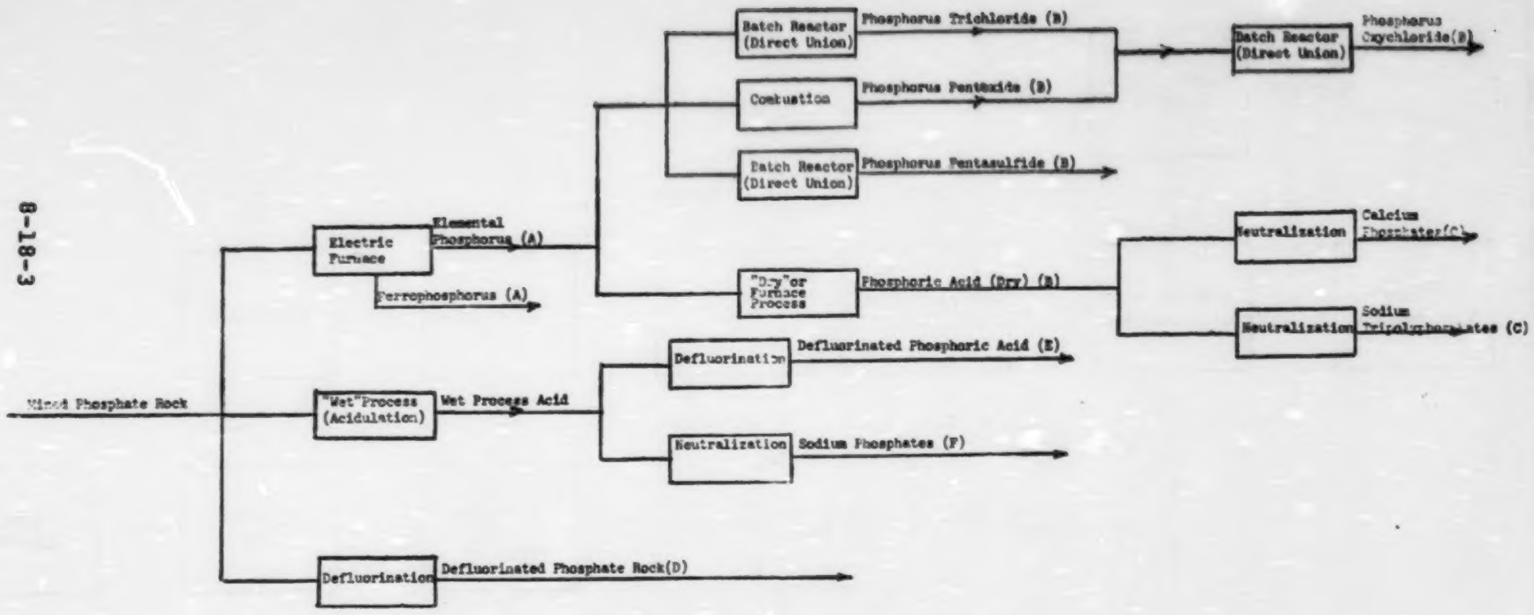

Mined Phosphate Rock
Electric Furnace
Elemental Phosphorus (A)
Ferrophosphorus (A)
"Wet" Process (Acidulation)
Wet Process Acid
Defluorination
Defluorinated Phosphate Rock(D)
Batch Reactor (Direct Union)
Phosphorus Trichloride (B)
Combustion
Phosphorus Pentoxide (B)
Batch Reactor (Direct Union)
Phosphorus Pentasulfide (B)
"Dry" or Furnace Process
Phosphoric Acid (Dry) (B)
Defluorination
Defluorinated Phosphoric Acid (E)
Neutralization
Sodium Phosphates (F)
Batch Reactor (Direct Union)
Phosphorus Oxychloride(B)
Neutralization
Calcium Phosphates(C)
Neutralization
Sodium Tripolyphosphates (C)

FIGURE 8-18-1
PHOSPHATE MANUFACTURING INDUSTRY
PRODUCT MANUFACTURING FLOW DIAGRAM

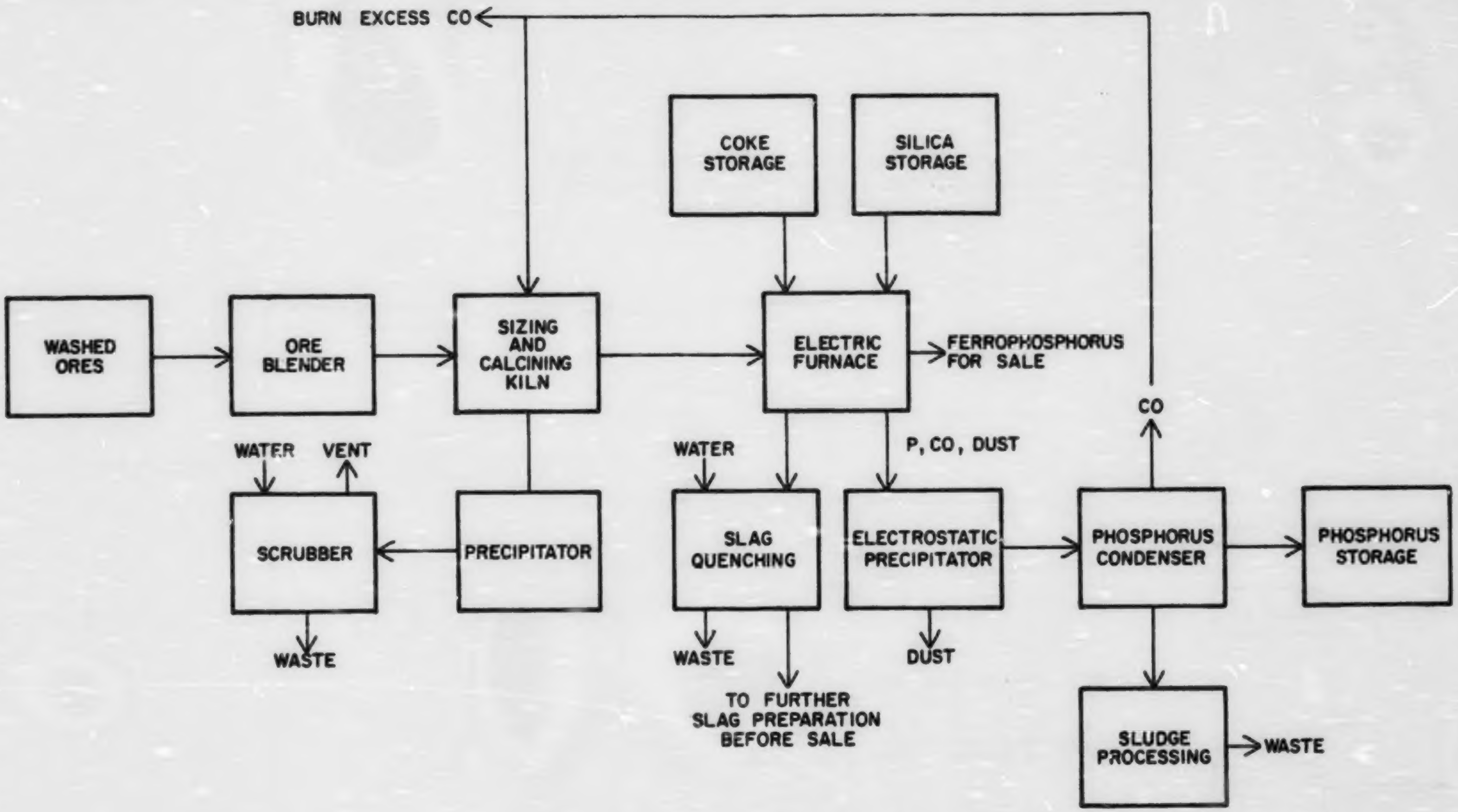

BURN EXCESS CO
COKE STORAGE
SILICA STORAGE
WASHED ORES
ORE BLENDER
SIZING AND CALCINING KILN
ELECTRIC FURNACE
FERROPHOSPHORUS FOR SALE
CO
WATER
VENT
WATER
P, CO, DUST
SCRUBBER
PRECIPITATOR
SLAG QUENCHING
ELECTROSTATIC PRECIPITATOR
PHOSPHORUS CONDENSER
PHOSPHORUS STORAGE
WASTE
WASTE
DUST
TO FURTHER SLAG PREPARATION BEFORE SALE
SLUDGE PROCESSING
WASTE

FIGURE 8-18-2
STANDARD PHOSPHORUS PROCESS FLOW DIAGRAM

CO and 10% phosphorus, pass through an electrostatic precipitator to remove the dust before phosphorus condensation. Downstream of the precipitator, the phosphorus is condensed by direct impingement of a hot water spray, sometimes augmented by heat transfer through water-cooled condenser walls. Liquid phosphorus drains into a water sump, where the water maintains a seal from the atmosphere. Liquid phosphorus is stored in steam-heated tanks under a water blanket and is transferred into tank cars by pumping or by hot water displacement. The tank cars have protective blankets of water and are equipped with steam coils for remelting at the destination.

There are numerous sources of fumes from the furnace operation. The feeding operation generates dust, and fumes are emitted from electrode penetrations and from tapping. These fumes, consisting of dust, phosphorus vapor (which is immediately oxidized to phosphorus pentoxide), and carbon monoxide are collected and scrubbed. Principal wastewater streams consist of calciner scrubber liquor, phosphorus condenser and other phossy water, and slag quenching water.

Phosphorus Consuming (B) - This subcategory embodies the following five products: phosphoric acid (dry process), phosphorus pentoxide, phosphorus pentasulfide, phosphorus trichloride, and phosphorus oxychloride. In the standard dry process for the production of phosphoric acid, liquid phosphorus is burned in the air, the resulting gaseous phosphorus pentoxide is absorbed and hydrated in a water spray, and the mist is collected with an electrostatic precipitator. Regardless of the process variation, phosphoric acid is made with consumption of water and no aqueous wastes are generated by the process.

Solid anhydrous phosphorus pentoxide is manufactured by burning liquid phosphorus in an excess of dried air in a combustion chamber. The vapor is condensed in a "barn" which is a room-like structure. Condensed phosphorus pentoxide is mechanically scraped from the walls using moving chains, and is discharged from the bottom of the barn with a screw conveyor. Phosphorus pentasulfide is manufactured by direct union of phosphorus and sulfur, both in liquid form. The highly exothermic reaction is carried out as a batch operation. Since the reactants and the product are highly flammable at the reaction temperature, the reactor is continuously purged with nitrogen. A water seal is used in the vent line.

Phosphorus trichloride is manufactured by charging liquid phosphorus into a jacketed batch reactor. Chlorine is bubbled through the charge, and phosphorus trichloride is refluxed until all the phosphorus is consumed. Cooling water is used in the reactor jacket and care is taken to avoid an excess of chlorine and the resulting formation of phosphorus pentachloride.

Phosphorus oxychloride is manufactured by the reaction of phosphorus trichloride, chlorine, and solid phosphorus pentoxide in a batch operation. Liquid phosphorus trichloride is charged to the reactor, solid phosphorus pentoxide is added, and chlorine is bubbled through the mixture. Steam is supplied to the reactor jacket, water to the reflux condenser is shut off, and the product is distilled over and collected.

Because phosphorus is transported and stored under a water blanket, phossy water is a raw waste material at phosphorus consuming plants. Another source of phossy water occurs if reactor contents containing phosphorus are dumped into a sewer line as a result of operator error, emergency conditions, or inadvertent leaks and spills.

Phosphate (C) - This subcategory embodies two product types: sodium tripolyphosphate and calcium phosphates. Sodium tripolyphosphate is manufactured by the neutralization of phosphoric acid in mix tanks by soda ash or by caustic soda and soda ash, with the subsequent calcining of the dried mono- and di-sodium phosphate crystals. The product is then slowly cooled or tempered to produce the condensed form of the phosphates.

The non-fertilizer calcium phosphates are manufactured by the neutralization of phosphoric acid with lime. Although the reactions are chemically similar, the processes for different calcium phosphates differ substantially in the amount and type of lime and the amount of process water used. Relatively pure, food grade monocalcium phosphate (MCP), dicalcium phosphate (DCP), and tricalcium phosphate (TCP) are manufactured in a stirred batch reactor from furnace grade acid and lime slurry, as shown in the process flow diagram of Figure 8-18-3. DCP is also manufactured for livestock feed supplement use, with much lower specifications on product purity.

Sodium tripolyphosphate manufacture generates no process wastes. Wastewaters from the manufacture of calcium phosphates are generated from dewatering of the phosphate slurry and wet scrubbing of the airborne solids during product drying operations.

Defluorinated Phosphate Rock (D) - Fluorapatite phosphate rock is the primary raw material for the defluorination process. Other raw materials used in much smaller amounts but critical to the process are sodium containing reagents, wet process phosphoric acid and silica. The charge is fed into either a rotary kiln or a fluid bed reactor. Fluid bed reactor requires a modular and pre-dried charge. Reaction temperatures are maintained in the 1205-1366°C range, while the retention time varies from 30 to 90

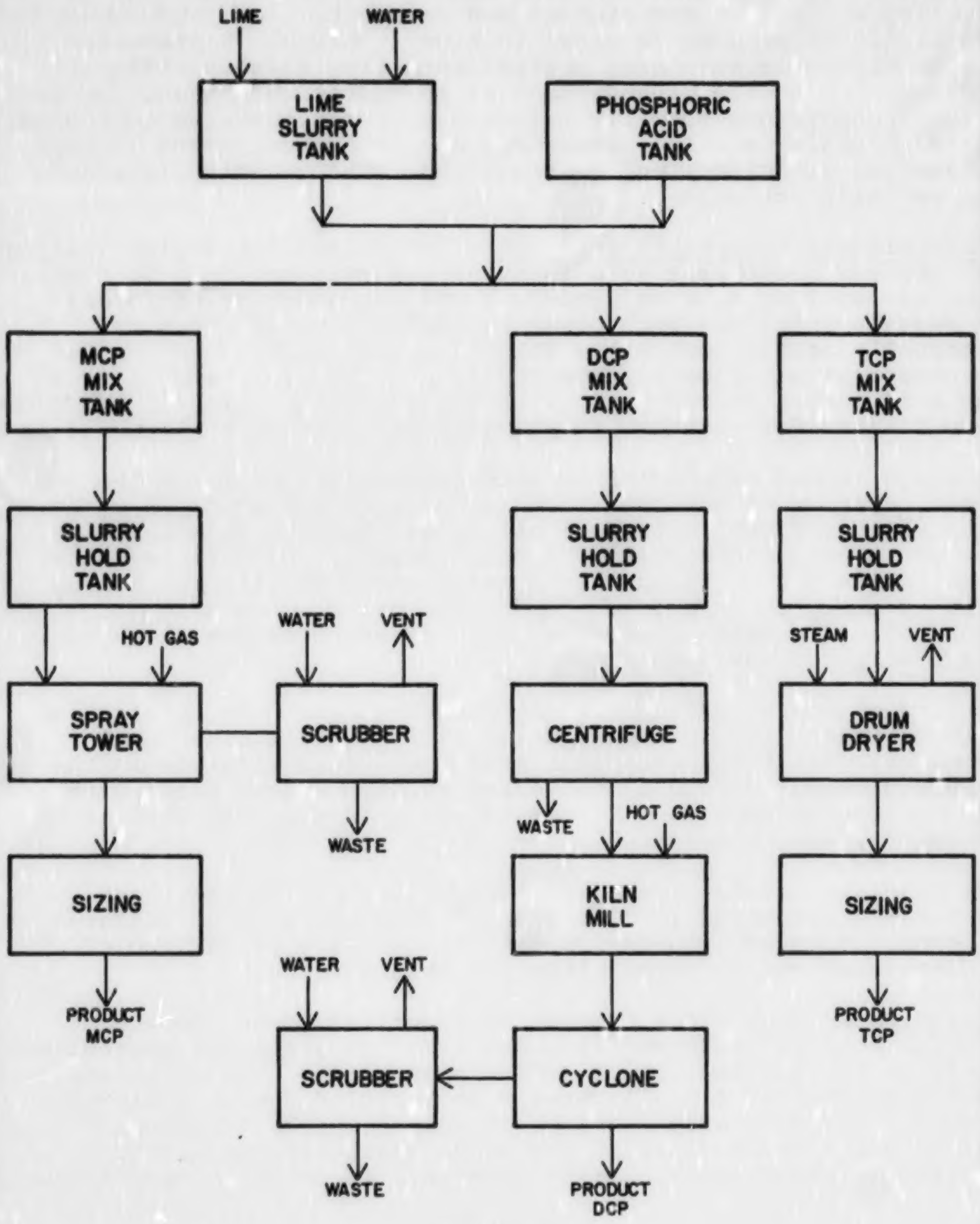

LIME
WATER
LIME SLURRY TANK
PHOSPHORIC ACID TANK
MCP MIX TANK
DCP MIX TANK
TCP MIX TANK
SLURRY HOLD TANK
SLURRY HOLD TANK
SLURRY HOLD TANK
HOT GAS
WATER
VENT
STEAM
VENT
SPRAY TOWER
SCRUBBER
CENTRIFUGE
DRUM DRYER
WASTE
WASTE
HOT GAS
SIZING
KILN MILL
SIZING
PRODUCT MCP
WATER
VENT
PRODUCT TCP
SCRUBBER
CYCLONE
WASTE
PRODUCT DCP

FIGURE 8-18-3
STANDARD PROCESS FOR
FOOD-GRADE CALCIUM PHOSPHATES

minutes. From the kiln or fluid bed reactor, the defluorinated product is quickly quenched with air or water, followed by crushing and sizing for storage and shipment. A flow diagram for the fluid bed process is shown in Figure 8-18-4. Wastewaters are generated in scrubbing contaminants from gaseous effluent streams. This water requirement is of appreciable magnitude and process conditions normally permit use of recirculated contaminated water for this service. Leaks and spills are collected as part of process efficiency and housekeeping. The quantity is minor and normally periodic.

Defluorinated Phosphoric Acid (E) - One method for defluorinating wet process phosphoric acid is by vacuum evaporation. Concentration of 54% P_2O_5 acid to a 68-72 % P_2O_5 strength is performed in vessels which use high pressure (450-550 psig) steam or externally heated Dowtherm solution as the heat energy source for evaporation of water from the acid. Fluorine removal from the acid occurs concurrently with the water vapor loss. A process flow diagram for vacuum type evaporation is shown in Figure 8-18-5.

A second method of phosphoric acid defluorination is by the direct contact of hot combustion gases with the acid. A combustion chamber fitted with fuel oil or gas burners is mounted on top of an acid containment chamber. Pressurized hot gases are bubbled through the acid. Evaporated and defluorinated product acid is sent to an acid cooler, while the gaseous effluents from the evaporation chamber flow to a series of gas cleaning and absorption equipment.

A third method of defluorinating phosphoric acid is by aeration. Diatomaceous silica or spray dried silica gel is mixed with commercial 54% P_2O_5 phosphoric acid. Hydrogen fluoride in the impure phosphoric acid is converted to fluosilicic acid which in turn breaks down to SiF_4 and is stripped from the heated mixture by simple aeration.

The major wastewater source in the defluorination processes is the wet scrubbing of contaminants from the gaseous effluent streams. However, process conditions normally permit use of recirculated contaminated water for this service.

Sodium Phosphates (F) - Removal of impurities from the wet process acid is performed in a series of separate neutralization steps in the manufacture of sodium phosphates. The first step is the removal of fluosilicates with recycled sodium phosphate liquor. The next step consists of adding sodium sulfide to the solution to precipitate the minor quantities of arsenic present. Concurrently, barium carbonate is added to remove the

DEFLUORINATED PHOSPHATE ROCK
FLUID BED PROCESS

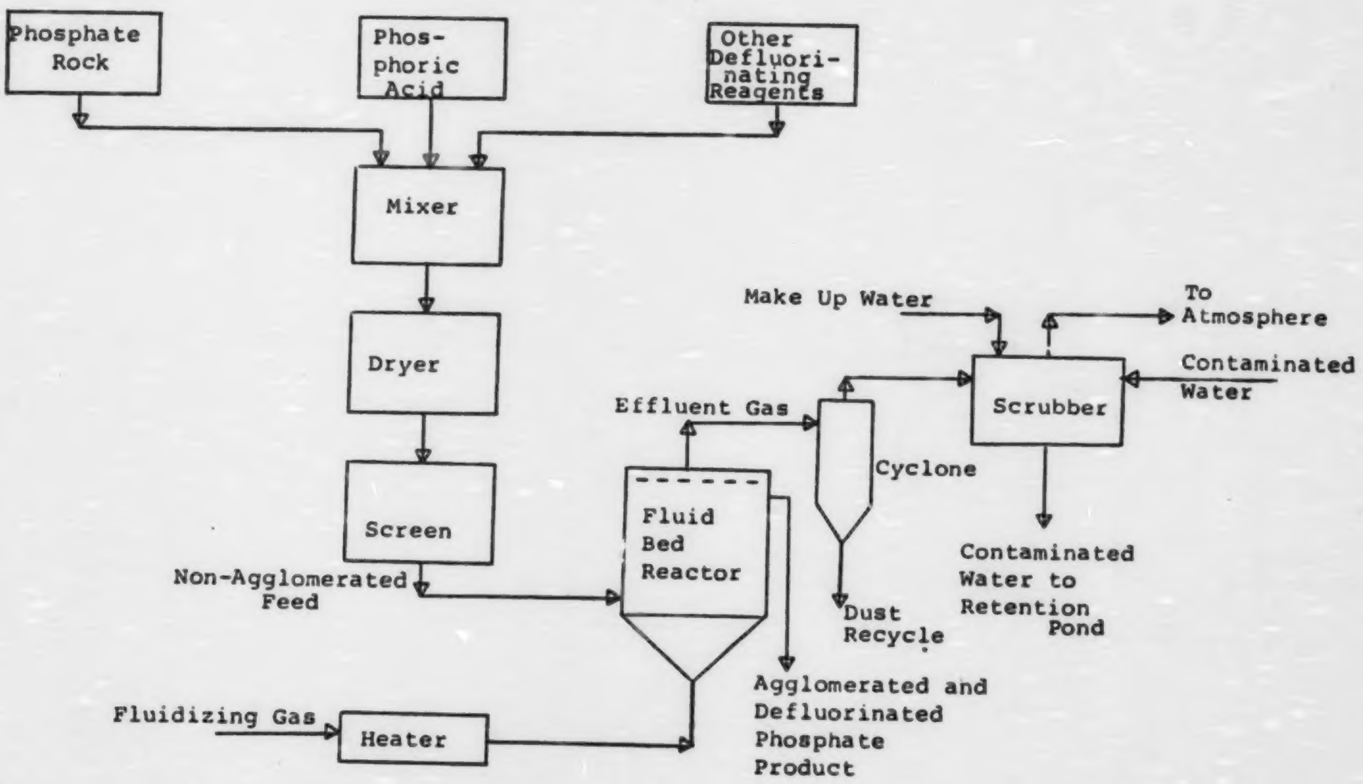

Phosphate Rock
Phos-phoric Acid
Other Defluori-nating Reagents
Mixer
Dryer
Screen
Non-Agglomerated Feed
Fluidizing Gas
Heater
Fluid Bed Reactor
Effluent Gas
Cyclone
Dust Recycle
Agglomerated and Defluorinated Phosphate Product
Make Up Water
Scrubber
To Atmosphere
Contaminated Water
Contaminated Water to Retention Pond

FIGURE 8-18-4

DEFLUORINATED PHOSPHORIC ACID - VACUUM PROCESS
(Super Phosphoric)

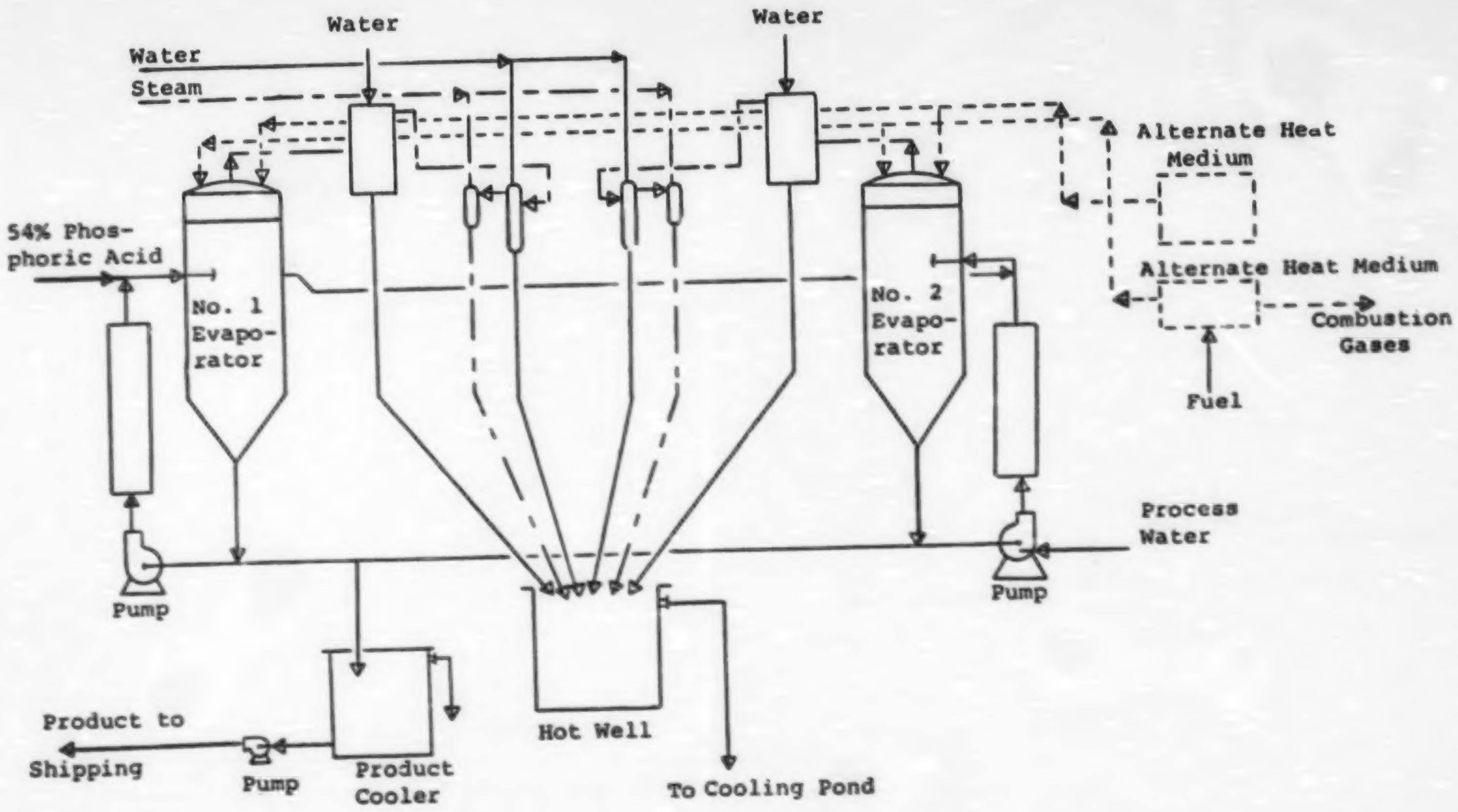

Water
Water
Water
Steam
Alternate Heat Medium
54% Phosphoric Acid
No. 1 Evaporator
No. 2 Evaporator
Alternate Heat Medium
Combustion Gases
Fuel
Process Water
Pump
Pump
Product to Shipping
Pump
Product Cooler
Hot Well
To Cooling Pond

FIGURE 8-18-5

excess sulfate. The partially neutralized acid still contains iron and aluminum phosphates, and some residual fluorine. A second neutralization is carried out with soda ash to a pH level of about 4.0. Special heating, agitation, and retention techniques are next employed to adequately condition the slurry so that filtration separation of the impurities can be accomplished. The remaining solution is sufficiently pure for the production of monosodium phosphate which can be further converted into other compounds such as sodium metaphosphate, disodium phosphate, and tri-sodium phosphate. A process flow diagram is shown in Figure 8 -18-6. Wastewater effluents from these processes originate from leaks and spills, filtration washes, and gas scrubber liquors.

4. Wastewater Characterization

Wastewater characteristics of process effluents from each of the 6 subcategories of the phosphate manufacturing industry are shown in Tables 8-18-1 and 8-18-2.

5. Control and Treatment Technology

In-Plant Control

Significant in-plant control of both waste quantity and quality is possible for most subcategories of the phosphate manufacturing industry. Important control measures include stringent in-process abatement, good housekeeping practices, containment provisions, and segregation practices. In the phosphorus chemicals industry (A,B,C), plant effluent can be segregated into non-contact cooling water, process water, and auxiliary streams comprising ion exchange regenerants, cooling tower blowdowns, boiler blowdowns, leaks and washings. Many plants have accomplished the desired segregation of these streams, often by a painstaking rerouting of the sewer lines. The widespread use of once-through scrubber waste should be discouraged. However, there are several plants notable in this respect which recycle the scrubber water from a sump, thus satisfying the scrubber water flow rate demands on the basis of mass transfer considerations while retaining control of water usage.

The containment of phossy water from phosphorus transfer and storage operations is an important control measure in the phosphorus consuming subcategory (B). While displaced phossy water is normally shipped back to the phosphorus-producing facility, the current practice in phosphorus storage tanks is to maintain a water blanket over the phosphorus for safety reasons. This practice is undesirable because the addition of

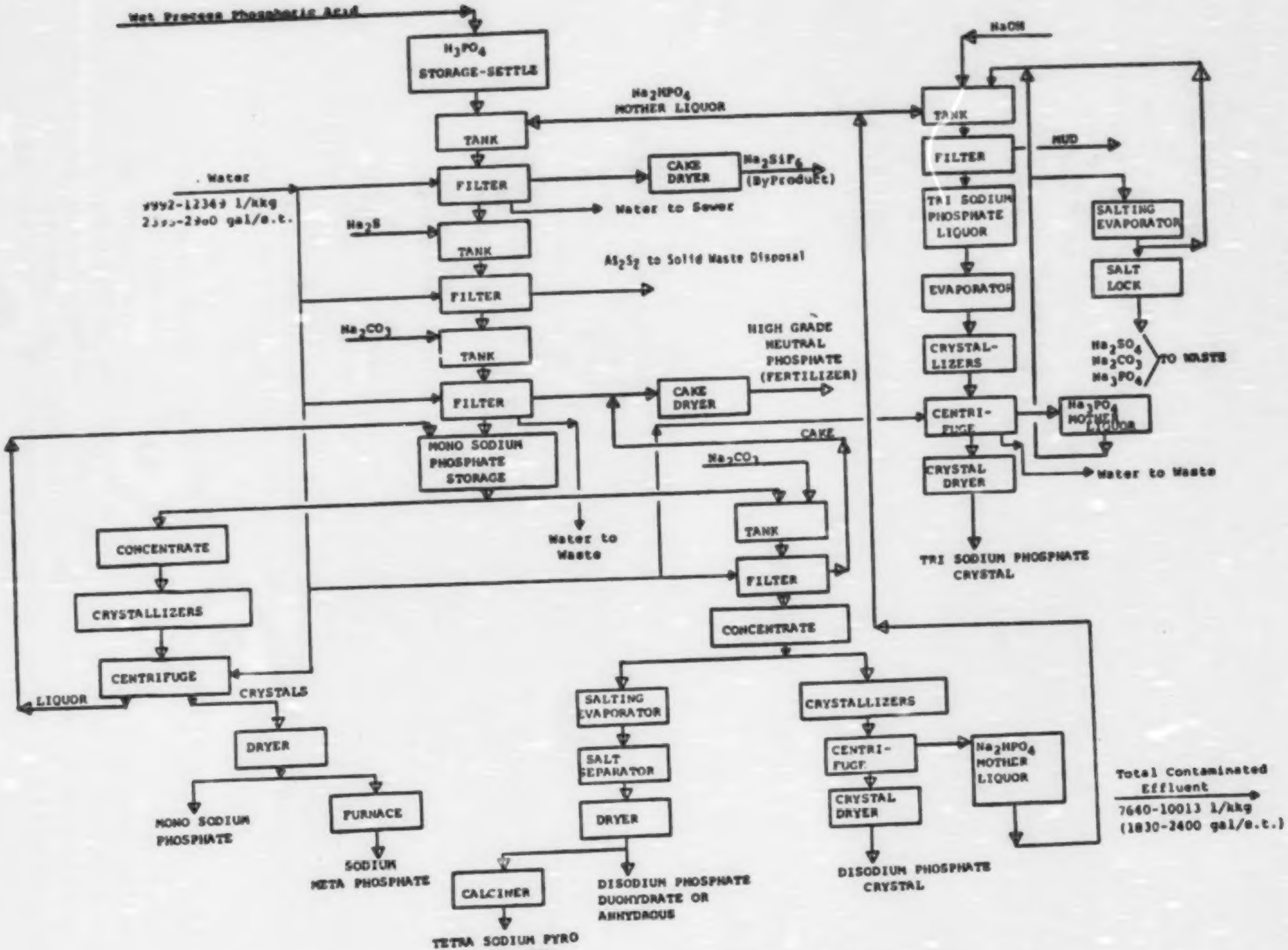

Wet Process Phosphoric Acid
H_3PO_4 STORAGE-SETTLE
TANK
Na_2HPO_4 MOTHER LIQUOR
Water
9992-12349 l/kkg
2395-2960 gal/s.t.
FILTER
CAKE DRYER
Na_2SiF_6 (ByProduct)
Water to Sewer
Na_2S
TANK
As_2S_3 to Solid Waste Disposal
FILTER
Na_2CO_3
TANK
FILTER
CAKE DRYER
HIGH GRADE NEUTRAL PHOSPHATE (FERTILIZER)
MONO SODIUM PHOSPHATE STORAGE
CAKE
Na_2CO_3
TANK
FILTER
Water to Waste
CONCENTRATE
CRYSTALLIZERS
CENTRIFUGE
LIQUOR
CRYSTALS
DRYER
MONO SODIUM PHOSPHATE
FURNACE
SODIUM META PHOSPHATE
CONCENTRATE
SALTING EVAPORATOR
SALT SEPARATOR
DRYER
CALCINER
TETRA SODIUM PYRO PHOSPHATE
DISODIUM PHOSPHATE DUOHYDRATE OR ANHYDROUS
CRYSTALLIZERS
CENTRI-FUGE
CRYSTAL DRYER
DISODIUM PHOSPHATE CRYSTAL
Na_2HPO_4 MOTHER LIQUOR
NaOH
TANK
FILTER
MUD
TRI SODIUM PHOSPHATE LIQUOR
SALTING EVAPORATOR
SALT LOCK
Na_2SO_4
Na_2CO_3
Na_3PO_4
TO WASTE
EVAPORATOR
CRYSTAL-LIZERS
CENTRI-FUGE
Na_3PO_4 MOTHER LIQUOR
CRYSTAL DRYER
Water to Waste
TRI SODIUM PHOSPHATE CRYSTAL
Total Contaminated Effluent
7640-10013 l/kkg
(1830-2400 gal/s.t.)

FIGURE 8-18-6
SODIUM PHOSPHATE PROCESS
From Wet Process
Phosphoric Acid

TABLE 8-18-1

PHOSPHATE MANUFACTURING INDUSTRY RAW WASTE CHARACTERIZATION

PARAMETER (mg/l)	PHOSPHORUS PRODUCTION A	PHOSPHORUS CONSUMING B	PHOSPHATE C	DEFLUORINATED PHOSPHATE ROCK D	DEFLUORINATED PHOSPHORIC ACID E	SODIUM PHOSPHATE F
Flow Type	C	B	B	B	B	B
BOD_5				3	15	31
SS	100		24,000-54,000	16	30	460
TDS			1,900-7,000*	2,250*	28,780*	1640*
COD				48	306	55
pH				1.65*	1.29*	7.8
Phosphorus	21					
PO4	59		7000*			
SO4	260			350	4,770	240
F	126			1,930	967	15
HCl		0-800				
H_2SO_3		0-34				
$H_3PO_3 + H_3PO_4$		17-500				
HF, H_2SiF_6, H_2SiO_3			1900*			
Chloride				101	65	90
Calcium				40	1700*	95
Magnesium				12	106	
Aluminum				58	260	
Iron				8*	180*	
Arsenic				0.38*	0.83*	
Zinc				5.2*	5.3*	
Total Acidity	128					
Total Phosphorus				600	5,590*	250

*See Appendix 5 for parameters which may be inhibitory to biological systems.
B - Batch Process
C - Continuous Process

TABLE 8-18-2

PHOSPHATE MANUFACTURING INDUSTRY RAW WASTE CHARACTERIZATION - PRODUCTION BASED DATA

PARAMETER (kg/kkg)	PHOSPHORUS PRODUCTION A	PHOSPHORUS CONSUMING B	PHOSPHATE C	DEFLUORINATED PHOSPHATE ROCK D	DEFLUORINATED PHOSPHORIC ACID E	SODIUM PHOSPHATE F
Flow Range (1/kkg)	425,000	38,000	10,920	45,890	18,020-70,510	7,640-10,020
Flow Type	C	B	B	B	B	B
BOD_5					0.27-1.06	0.2-0.3
SS	42.5		22.5-50	0.73	0.54-2.11	3.5-4.6
TDS			4.0-14.6	103	519-2,031	12.5-16.40
COD				2.2	5.5-21.5	0.4-0.52
pH				1.65	1.29	7.8
Phosphorus	9					
PO_4	25		15			
SO_4	111			16	86-336	1.8-2.36
F	53.5			88	17.4-68.1	0.1-0.13
HCl		0-3				
H_2SO_3		0-1.0				
$H_3PO_3 + H_3PO_4$		0.5-2.5				
HF, H_2SiF_6, H_2SiO_3			12			
Chloride				4.6	1.17-4.58	0.68-0.90
Calcium				1.8	30.6-120	0.72-0.94
Magnesium				0.6	1.9-7.43	
Aluminum				2.7	4.7-18.39	
Iron				0.37	3.2-12.52	
Arsenic				0.02	0.02-0.08	
Zinc				0.24	0.09-0.35	
Total Acidity*	54.5					
Total Phosphorus				27.5	101-395	1.91-2.51

makeup water often results in the discharge of phossy water. One way to ensure zero discharge of phossy water is to install an auxiliary tank to collect phossy water overflows from the storage tanks. A closed-loop system is then possible if the phossy water from the auxiliary tank is reused as makeup for the main phosphorus tank. Another special problem in the phosphorus consuming subcategory (B) is the inadvertent spills of elemental phosphorus into the plant sewer line. Provision should be made for collecting, segregating, and bypassing such spills. A recommended control measure is the installation of a trap of sufficient volume just downstream of reaction vessels. In the phosphates subcategory (C), an important area of concern is the pickup by stormwater of dust originating from the handling, storing, conveying, sizing, packaging and shipping of finely-divided solid products. Airborne dusts can be minimized through air pollution abatement practices. Stormwater pickup should be further controlled through strict dust cleanup programs.

In the defluorinated phosphate rock (D) and defluorinated phosphoric acid (E) subcategories, water used in scrubbing contaminants from the gaseous effluent stream constitutes a significant part of the process water requirements. In both subcategories, process conditions do permit use of contaminated water for this service. Some special precautions are essential at a plant producing sodium phosphates (F). All meta, tetra, pyro and polyphosphate wastewater in spills should be diverted to the reuse pond. These phosphates do not precipitate satisfactorily in the lime treatment process and interfere with the removal of fluoride and suspended solids. Since unlined ponds are the most common treatment facility in the phosphate manufacturing industry, prevention of pond failure is vitally important. Failures of these ponds sometimes occur because they are unlined and because they may be improperly designed for containment in times of heavy rainfall. Design criteria for ponds and dikes should be based on the anticipated rainfall and drainage requirements. Failure to put in toe drainage in dikes is a major problem. Massive contamination from dike failure is the major concern for industries utilizing ponds.

Treatment Technology

The various wastewater treatment practices for each of the six subcategories of the phosphate manufacturing industry are summarized in Table 8-18-3. The removal efficiencies shown pertain to the raw waste loads of process effluents from each of the subcategories.

TABLE 8-18-3

PHOSPHATE MANUFACTURING INDUSTRY
WASTEWATER TREATMENT PRACTICES
REMOVAL EFFICIENCIES (PERCENT)

POLLUTANT AND METHOD	PHOSPHORUS PRODUCTION A	PHOSPHORUS CONSUMING B	PHOSPHATE C	DEFLUORINATED PHOSPHATE ROCK D	DEFLUORINATED PHSOPHORIC ACID E	SODIUM PHOSPHATE F
TDS						
1. Lime Treatment and Sedimentation*	99		99			
TSS						
1. Lime Treatment and Sedimentation*	99		99			
2. Flocculation, Clarification and Dewatering		92				
TOTAL PHOSPHATE						
1. Lime Treatment and Sedimentation*	97	73-97	97			
PHOSPHORUS						
1. Lime Treatment and Sedimentation*				90	99	88
2. Flocculation, Clarification and Dewatering		92				
SULFATE						
1. Lime Treatment and Sedimentation*	98		98			
FLUORIDE						
1. Lime Treatment and Sedimentation*	99		99	98	96	0
pH (Effluent Level)						
1. Lime Treatment and Sedimentation* (Neutralization)				6-8	6-8	6-8

*Preceded by recycle of phossy water and evaporation of some process water in Subcategories A, B and C.

1. Industry Description

Steam electric power plants are the production facilities of the electric power industry. The industry also provides for the transmitting and distribution of electric energy.

Unlike other industries, the product, electricity, cannot be stored, and therefore, the industry must be ready to produce at any given time all the product that the consumer desires.

Four (4) basic fuels are used in steam electric power plants. They are: coal, natural gas, oil and uranium. The fuel is used to generate heat, which converts water to steam. The steam is then used to turn a steam turbine (producing mechanical energy). The turbine in turn conveys the mechanical energy to a generator converting mechanical energy to electric energy. Wastewaters generally contain heat, chemicals and metals.

This industry is designated by Standard Industrial Classifications (SIC) 4911 and 4931.

2. Industrial Categorization

The subcategorization of the power industry is generally based upon the age and size of the plant:

Generating Unit	(A)
Small Unit	(B)
Old Unit	(C)
Area Run-off	(D)

Generating Unit (A) - All units not classified as Old (C) or Small (B).

Small Unit (B) - All units generating less than 25 megawatts except those classified as Old (C). In addition, any unit which is part of an electric utilities system with a total net generating capacity of less than 150 megawatts.

Old Unit (C) - All units generating 500 megawatts or greater which were first placed in service on or before January 1, 1970. Also, all units generating less than 500 megawatts which were first placed in service on or before January 1, 1974.

Area Runoff (D) - Discharges resulting from material storage runoff and construction runoff that are associated with generation (A,B,C).

3. Process Description

As noted above, the subcategories have generally been based upon age and size of plants. However, the process of generating electricity is the same for all subcategories, and therefore, the wastes produced are similar. Discussions below will, therefore, be based on the unit processes in power plants rather than subcategories.

There are five (5) major unit processes involved in the generation of electric power. They are:

(1) Storage and handling of fuel related materials, both before and after use.

(2) Production of high-pressure steam.

(3) Expansion of the steam in a turbine, which drives the generator.

(4) Condensation of the steam leaving the turbine.

(5) Generation of electric energy by the generator.

Refer to the flow diagrams in Figures 8-19-1 and 8-19-2.

Materials Storage and Handling - (1) All fuels must be delivered to the plant site, stored until used, and the spent fuel materials stored on the premises.

Storm runoff from coal piles and oil spills from oil storage can be sources of wastes. Contact of coal with air and moisture results in oxidation of metal sulfides present in coal, to sulfuric acid. Liquid drainage from coal storage piles presents a potential danger of pollution. Sometimes these piles are sprayed with tar to seal the outer surface. Ground seepage can be minimized by storing the coal on an impervious vinyl liner.

Coal pile runoff is commonly characterized as low pH, and high in dissolved solids. High concentrations of metals may also be present.

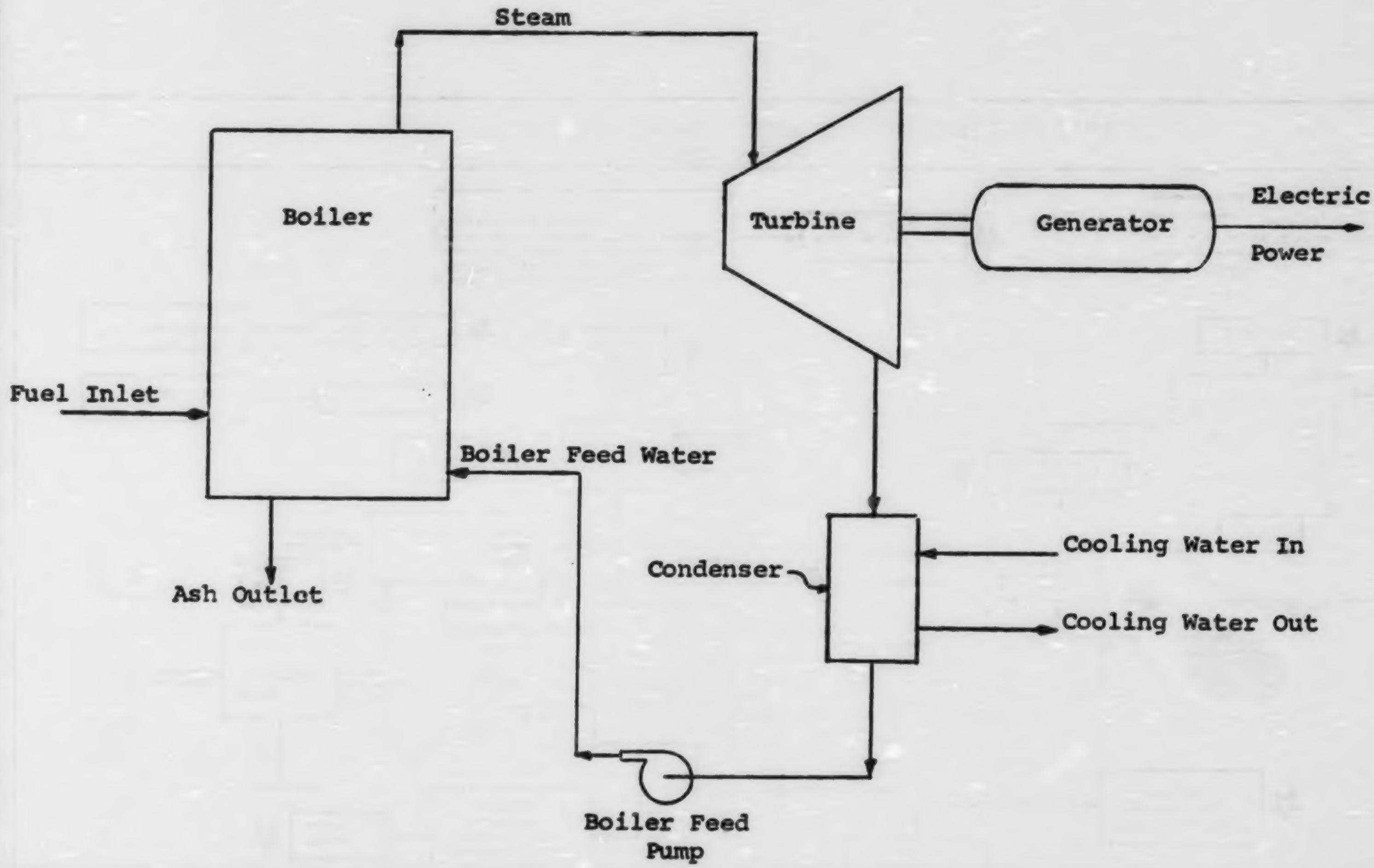

Steam
Boiler
Turbine
Generator
Electric
Power
Fuel Inlet
Boiler Feed Water
Ash Outlet
Condenser
Cooling Water In
Cooling Water Out
Boiler Feed
Pump

Figure 8-19-1
Process Flow Diagram
Steam Electric Power Industry

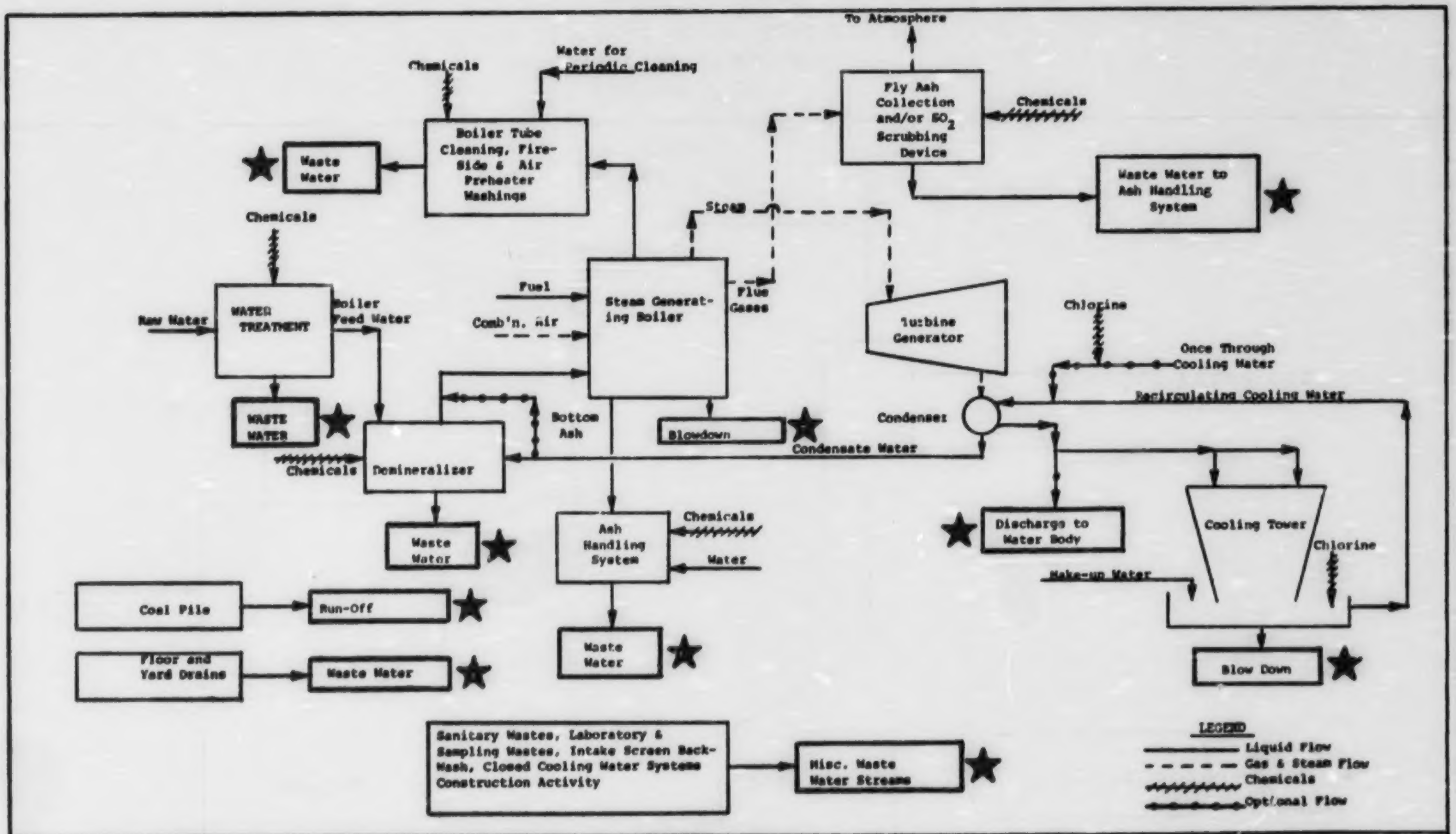

To Atmosphere
Chemicals
Water for Periodic Cleaning
Boiler Tube Cleaning, Fire-Side & Air Preheater Washings
Waste Water
Fly Ash Collection and/or SO2 Scrubbing Device
Chemicals
Waste Water to Ash Handling System
Chemicals
Raw Water
WATER TREATMENT
Boiler Feed Water
WASTE WATER
Steam
Fuel
Comb'n. Air
Steam Generating Boiler
Flue Gases
Turbine Generator
Chlorine
Once Through Cooling Water
Recirculating Cooling Water
Condenser
Bottom Ash
Blowdown
Condensate Water
Chemicals
Demineralizer
Waste Water
Ash Handling System
Chemicals
Water
Waste Water
Discharge to Water Body
Cooling Tower
Chlorine
Make-up Water
Blow Down
Coal Pile
Run-Off
Floor and Yard Drains
Waste Water
Sanitary Wastes, Laboratory & Sampling Wastes, Intake Screen Back-Wash, Closed Cooling Water Systems Construction Activity
Misc. Waste Water Streams
LEGEND
Liquid Flow
Gas & Steam Flow
Chemicals
Optional Flow

FIGURE 8-19-2
TYPICAL FLOW DIAGRAM - STEAM ELECTRIC POWER(FOSSIL-FUELED)

The fuels are transported from the storage facilities to the furnace where combustion takes place. Combustion generates non-combustible residues called ash. The portion of ash carried along with the hot gases is called fly ash, and the portion that settles to the bottom of the furnace is called bottom ash. Coal produces a relatively large amount of bottom ash. Oil produces little bottom ash, but substantial amounts of fly ash. Natural gas produces little ash of any type.

Ash may be conveyed to the disposal site by either wet or dry means. Most utilities have installed a sedimentation facility to handle coal ash, whereas oil ash may be recycled into the furnace or removed by water washing. Since there is a large variation in fuel quality, wastewater concentrations may vary considerably. Some ash sluice waters contain significant concentrations of metals.

The radioactive wastes generated in a nuclear power plant are handled internally. The low level radioactive discharges are carefully regulated.

Steam Production (2) - Feed water is introduced into the boiler feed pump and first enters a series of tubes near the point where the gases are exiting the boiler. The water is heated by the existing gases, which in turn cools the gases. The water then flows to one or more drums connected by a series of tubes. These tubes are arranged vertically along the combustion zone of the boiler, where the water is converted to steam. The water and steam are separated in the boiler drum, and the steam leaving the drum is heated further in the superheater section of the boiler. The superheated steam then leaves the boiler and passes to the turbine. The boiler drum is purged periodically to prevent build-up of impurities in the boiler. This waste stream will contain heavy metals and corrosion inhibitor chemicals used in the system.

Due to losses in the steam cycle, such as boiler blow-down, water must be added to the system as replacement. Since the steam cycle requires high quality water, the "make-up" water must be demineralized (de-ionized). The regeneration of the demineralizers constitues a waste stream which will be high in dissolved solids with either very low or very high pH values. In many cases, the make-up water is "pretreated" before demineralization, by clarification and filtration. This will provide clarifier sludges and filter backwash streams.

Periodically the boiler will be chemically cleaned to remove scale and corrosion products from the boiler tubes. The wastewater produced from this procedure will be high in heavy metals, spent acid and caustic solutions, oil and grease, and extreme pH values.

In addition to chemically cleaning the boiler tubes, other sections of the boiler will be cleaned, such as the air preheater and the fire side of the tubes, which will produce waste streams high in oil and grease, suspended solids, spent chemicals, and extreme pH values.

Steam Expansion (3) - The steam expands in the turbine converting the pressure energy to mechanical energy. By superheating the steam to a proper point, the expansion will take place with only small amounts of the steam condensing to water in the turbine.

In many power plants, there are two turbines in series, one high pressure, and one low pressure. The steam exiting the high pressure turbine is reheated in the boiler before entering the low pressure turbine. No waste products are associated with this process.

Steam Condensation (4) - The steam leaving the turbine is condensed in a heat exchanger, or condenser, creating a low turbine exhaust pressure. The condensing actually causes a vacuum condition, creating high energy conversion efficiencies in the turbine. The condensed steam is then repumped to the boiler, completing the cycle.

The condenser is basically a shell and tube heat exchanger with water being used as the coolant. The cooling system can either be of the once-through or closed cycle type. In the once through system, water is drawn from a large body of water such as a river or lake, passed through the condenser and returned to the receiving body.

In the closed cooling system, the cooling water leaving the condenser is cooled in a cooling tower or cooling pond and then recycled back to the condenser.

In the once-through system, high volumes of water are used, and the only waste associated with it are heat, and free available chlorine. (Chlorine is used to inhibit biological growth in the condenser system).

In the closed system the cooling tower will be periodically purged to prevent build-up of dissolved solids, and this blowdown stream will contain scaling inhibitors used in the cooling tower, turbidity and dissolved solids.

Generation of Electricity (5) - The turbine is directly connected to a generator, which converts mechanical energy to electric energy at almost 100% of theoretical efficiency. There are no wastes associated with this process.

4. Wastewater Characteristics

See Table 8-19-1 for wastewater characteristics of the industry.

5. Control and Treatment Technology

As indicated in Table 8-19-1, many wastewater streams are produced in batches which contain extreme pH ranges. Equalization and batch treatment facilities can provide simple economical removals of oil & grease and heavy metals, and also prevent large wastewater fluctuations to the municipal system.

Alternate water treatment schemes can be instituted if metal-containing water treatment chemicals cause treatment problems.

Wastewater flow rates can be reduced through increased recycling. Table 8-19-2 contains percentage removals of pollutants by various treatment methods.

TABLE 8-19-1
RAW WASTEWATER CHARACTERIZATION
STEAM ELECTRIC POWER INDUSTRY

PARAMETER mg/l	OPERATION									
	Water Treatment					Cleaning Wastes				
	Clarification Wastes	Ion-Exchange Wastes	Boiler Blowdown	Cooling Tower Blowdown	Coal Pile Drainage	Boiler Tubes	Air Preheater	Boiler Fireside	Ash Pond Overflow	Yard & Floor Drains
Flow Range (gpd)	10 - 10M	1M - 80M	1M - 30M	30M - 2MM	800 - 3M	80M - 400M	50M - 3MM	20M - 1MM	3MM - 5MM	1M - 5M
Flow Type	C	B	C	B	B	B	B	B	C	B
BOD	0 - 60	1 - 100	0 - 5	0 - 100	No Data	0 - 100	0 - 6	1 - 6	No Data	2 - 4
TSS	10 - 140 M	0 - 200	0 - 20	10 - 500	No Data	150 - 2500	200 - 2M	200 - 700	1 - 100	0 - 5
COD	0 - 1M	0 - 100	0 - 40	1 - 500	No Data	1M - 3M	20 - 200	100 - 200	No Data	No Data
pH	Neutral - High	Low and High	Neutral - High	Neutral	2 - 8	Low & High	Low & High	Low & High	No Data	Low - Neutral
Surfactants						Present			Present	Present
Chromium	0 - 3*	0 - 1	0 - 2	0 - 0.1	No Data	0.2 - 6*	6 - 12*	0 - 5*	0 - 0.1	0 - 20*
Copper	0 - 2*	0 - 3*	0 - 2.0	0 - 2*	1 - 4*	50 - 200*	5 - 10*	NIL	NIL	No Data
Iron	0 - 1500*	0 - 40*	0 - 2.0	0 - 1	0.1 - 5M*	50 - 500*	2 - 1,000*	50 - 150*	0.3	No Data
Lead					Present				Present	Present
Manganese		0 - 1		0 - 0.1					NIL	
Mercury		Present			Present	Present			Present	
Nickel	0 - 1	0 - 1	0 - 0.1	0 - 1		80*	50 - 75*	5*	NIL	
Selenium					Present	Present			Present	
Vanadium							Present	Present	Present	
Zinc	0 - 5*	0 - 4.5*	0 - 1*	0 - 3*	1 -15*	20 - 50*	5*	5 - 10*	0 - 0.1	0 - 10*
Phosphorous	0 - 20	0 - 90	0 - 50	2 - 20	NIL	0.2 - 4	1 - 2	0 - 2	0 - 0.5	No Data
Phenols	Present	NIL	0 - 0.5	0 - 0.1	Present				Present	
Ammonia	0 - 1	0 - 400	0 - 2	0 - 1	No Data	1 - 15	2 - 6	0 - 1	0 - 20	
Oil and Grease		0 - 25				Present	Present	Present		Present

M	thousand
MM	million
C	continuous
B	batch
*	See Appendix 5 for parameters which may be inhibitory to biological systems.

TABLE 8-19-2

STEAM ELECTRIC POWER
WASTEWATER TREATMENT PRACTICES

Pollutant and Treatment Method	% Removal
Oil & Grease	
Gravity Separator	50-70%
Gravity Separator + Filtration	70-90%
Metals	
Neutralization and Precipitation	50-95%

1. General Industry Description

This industry manufactures ferroalloys, a material which constitutes a crude alloy of iron with some other metal, and is used as an addition agent or alloying material in the production of steel and other metals. Manganese is the most widely used addition element in ferroalloys, followed by silicon and chromium. Others include molybdenum, tungsten, titanium, zirconium, vanadium, boron, and columbium. Principal products include: silvery iron, ferrosilicon, silicon metal, ferromanganese, silicomanganese, ferromanganese silicon, charge chrome, ferrochromium, ferrochrome silicon, manganese metal, magnesium ferrosilicon, ferrotitanium, titanium alloys, vanadium alloys, columbium alloys, calcium carbide, and chromium and manganese metals.

The largest source of waterborne pollutants other than thermal in this industry is the use of wet methods for air pollution control. Production of ferroalloys has many dust and fume producing steps. Consideration of air pollution control devices is thus of crucial importance in determining the volume and pollutant parameters of various wastewater streams.

The ferroalloy manufacturing industry includes Standard Industrial Classifications(SIC) 3312, 3313.

2. Industrial Categorization

The ferroalloy manufacturing industry is broadly subdivided into three main categories: the smelting and slag processing segment, the calcium carbide segment, and the electrolytic ferroalloys segment. For the purposes of raw waste characterization and delineation of pretreatment information, the industry is further subdivided into seven subcategories as shown in Table 8-20-1.

3. Process Description

The various ferroalloy manufacturing processes along with the product groups manufactured by each process are listed in Table 8-20-2. The production of ferromanganese in blast furnaces is part of the steel making industry and is not considered herein. Calcium carbide (D,E) is manufactured by the thermal reduction of calcium oxide (lime) and coke in a submerged arc electric furnace. Electrolytic processes are used for manganese (F) and chromium (G). The other processes listed in Table 8-20-2 are used for the product groups in the smelting and slag processing segment (A,B,C) of the industry.

TABLE 8-20-1

FERROALLOY MANUFACTURING

Main Category	Subcategory	Designation
1. Smelting & Slag Processing	Open Electric Furnace with Wet Air Pollution Control Devices	(A)
	Covered Electric Furnaces and Other Smelting Operations with Wet Air Pollution Control Devices	(B)
	Slag Processing	(C)
2. Calcium Carbide	Covered Calcium Carbide Furnaces with Wet Air Pollution Control Devices	(D)
	Other Calcium Carbide Furnaces	(E)
3. Electrolytic Ferroalloys	Electrolytic Manganese Products	(F)
	Electrolytic Chromium	(G)

TABLE 8-20-2
FERROALLOY MANUFACTURING PROCESSES AND PRODUCT GROUPS

Manufacturing Process	Product Group
Submerged-arc furnace process	Silvery iron 50, 65-75 percent ferrosilicon Silicon metal Silicon-manganese-zicronium High-carbon(HC) ferromanganese Silicomanganese Ferromanganese silicon Charge chrome HC ferrochromium Ferrochrome silicon Calcium Carbide
Exothermic process	Low-carbon(LC) ferrochromium LC ferromanganese Medium Carbon (MC) ferromanganese Chromium metal Titanium, vanadium, and columbium alloys
Electrolytic process	Chromium metal Manganese metal
Vacuum furnace process	LC ferrochromium
Induction furnace process	Magnesium ferrosilicon Ferrotitanium

Open and Covered Electric Furnaces and Other Smelting Operations with Wet Air Pollution Control Devices (A, B)

The majority of electric ferroalloy furnaces are termed submerged arc, although the mode of energy release is often resistive heating. Raw ore, coke, and limestone or dolomite mixed in proper proportions constitute the charge for the furnace. The three electrodes are arranged in a delta formation with the tips submerged into the charge within the furnace crucible so that the reduction center lies in the middle of the charge and reaction gases pass upward. The molten alloy from the carbon reduction of the ore accumulates at the base of the electrodes in the furnace and is periodically removed through a tap hole. A smaller number of furnaces in the industry do not operate with deep submergence of the electrodes and produce a batch melt which is usually removed by tilting the furnace.

The conventional submerged arc furnace utilizes carbon reduction of metallic oxides and continuously produces large quantities of carbon monoxide (CO). Other sources of gas are moisture in the charge materials, reducing agent volatile matter, thermal decomposition products of raw ore, and intermediate reaction products. The carbon monoxide content of the furnace off-gas varies from 50-90 percent by volume, depending upon the alloy being produced and furnace feed pretreatment.

Submerged-arc furnaces operate under steady-state conditions and gas generation is continuous. In an open furnace, all the CO burns with induced air at the top of the charge. In a covered or closed furnace, most or all of the CO is withdrawn from the furnace without combustion with air. Fume emissions also occur at furnace tap holes. Because most furnaces are tapped intermittently, tap hole fumes occur only about 10-20 percent of the furnace operating time.

Ferroalloy production in submerged-arc furnaces consists of raw materials preparation and handling, smelting, and product sizing and handling as shown in Figure 8-20-1.

The exothermic processes using silicon or aluminum, or a combination of the two, are used less commonly than the submerged-arc processes. In the exothermic process, silicon or aluminum combines the oxygen of the charge, generating considerable heat and creating temperatures of several thousand degrees in the reaction vessel. The process is generally used to produce high grade alloys with low carbon content. A process flow diagram is shown in Figure 8-20-1 for the manufacture of low carbon ferrochromium.

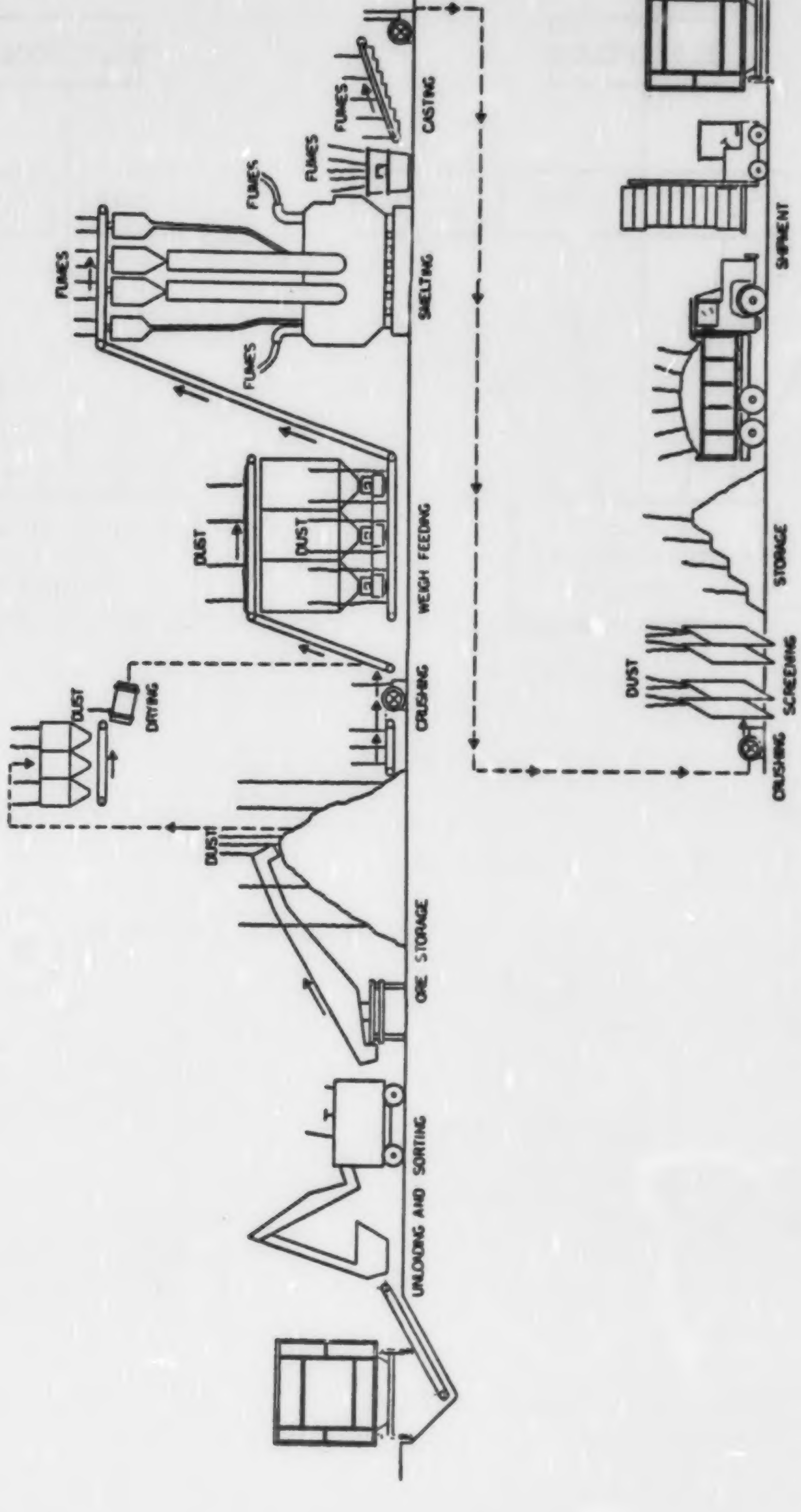

UNLOADING AND SORTING
ORE STORAGE
DUST
CRUSHING
DRYING
DUST
WEIGH FEEDING
DUST
DUST
FUMES
FUMES
FUMES
FUMES
FUMES
SMELTING
CASTING
CRUSHING
SCREENING
DUST
STORAGE
SHIPMENT

FIGURE 8-20-1
FERROALLOY PRODUCTION FLOW DIAGRAM

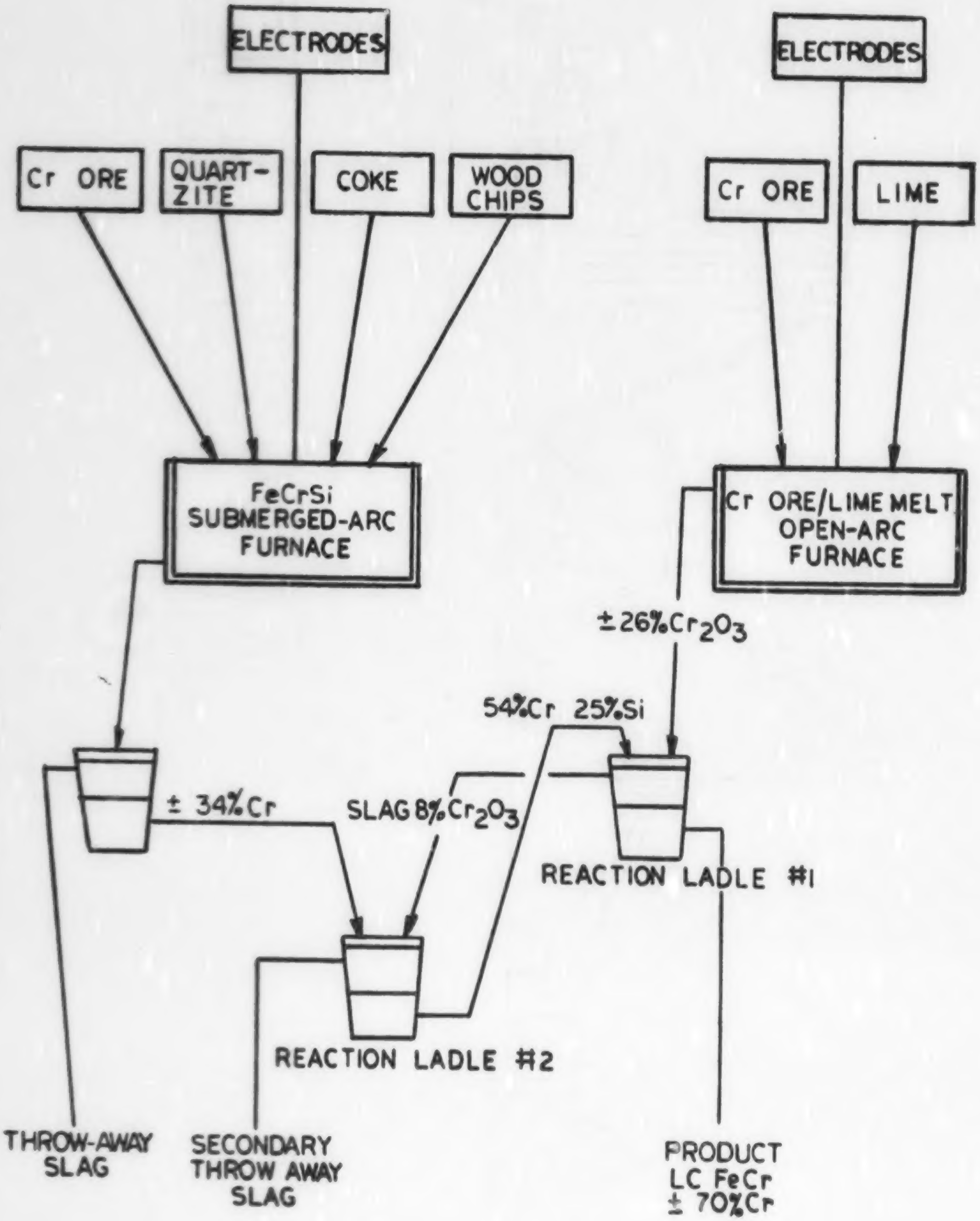

ELECTRODES
ELECTRODES
Cr ORE
QUARTZITE
COKE
WOOD CHIPS
Cr ORE
LIME
FeCrSi SUBMERGED-ARC FURNACE
Cr ORE/LIME MELT OPEN-ARC FURNACE
±26% Cr_2O_3
54%Cr 25%Si
± 34%Cr
SLAG 8% Cr_2O_3
REACTION LADLE #1
REACTION LADLE #2
THROW-AWAY SLAG
SECONDARY THROW AWAY SLAG
PRODUCT LC FeCr ± 70%Cr

FIGURE 8-20-2
FLOW SHEET LC FERROCHROMIUM

Air pollution control devices used in the electric furnace production of ferroalloys include baghouses, wet scrubbers, and electrostatic precipitators. Wet scrubbers generate slurries containing most of the particulates in the off-gases. Baghouses generally produce no wastewater effluents, except in one case where gases from exothermic processes are cooled by water sprays, scrubbed in wet dynamic scrubbers, and then cleaned in a baghouse where the bags are periodically washed with water. Spray towers used to cool and condition the gases before precipitators produce slurries containing some of the particulates in the gases. Wet scrubbers are the only APC device used on covered furnaces in this country. Electrostatic precipitators are in use on only two open furnaces producing ferrosilicon, ferrochromesilicon, high-carbon ferrochromium, and silicomanganese. Other sources of wastewater result from cooling uses, boiler feed, air conditioning and sanitary uses.

Slag Processing (C)

Some of the electric-arc smelting processes produce slag along with the ferroalloy product. These are: low carbon ferrochromesilicon, high carbon ferrochromium, high carbon ferromanganese, and silicomanganese. The entrapped metal in the slag is recovered by crushing and separation of the metal by the wet sink-float process, called slag concentration. The slag fines are also separated from the heavier particles so that the secondary product is slag of a size suitable for road building and similar purposes. This process is usually applied to ferrochromium slags for recovery of chromium which is recharged to the furnace. Another method consists of rapid quenching of the molten slag in a large volume of flowing water. This produces a small-sized particle (shot) which can be readily leached with acid to produce the electrolyte solution for electrolytic ferroalloy manufacture. Suspended solids,chromium and manganese are the important pollutants contained in slag processing wastewaters.

Calcium Carbide Furnaces (D, E)

Calcium carbide is manufactured by the thermal reduction of calcium oxide (lime) and coke in a submerged-arc electric furnace. A process flow diagram for the covered furnace calcium carbide manufacture is shown in Figure 8-20-3. The only source of process water pollutants is the use of wet air pollution control devices such as scrubbers. Wastewaters typically include suspended solids, cyanide, iron, silicon and calcium. Use of dry air pollution control devices result in zero discharge of process wastewater.

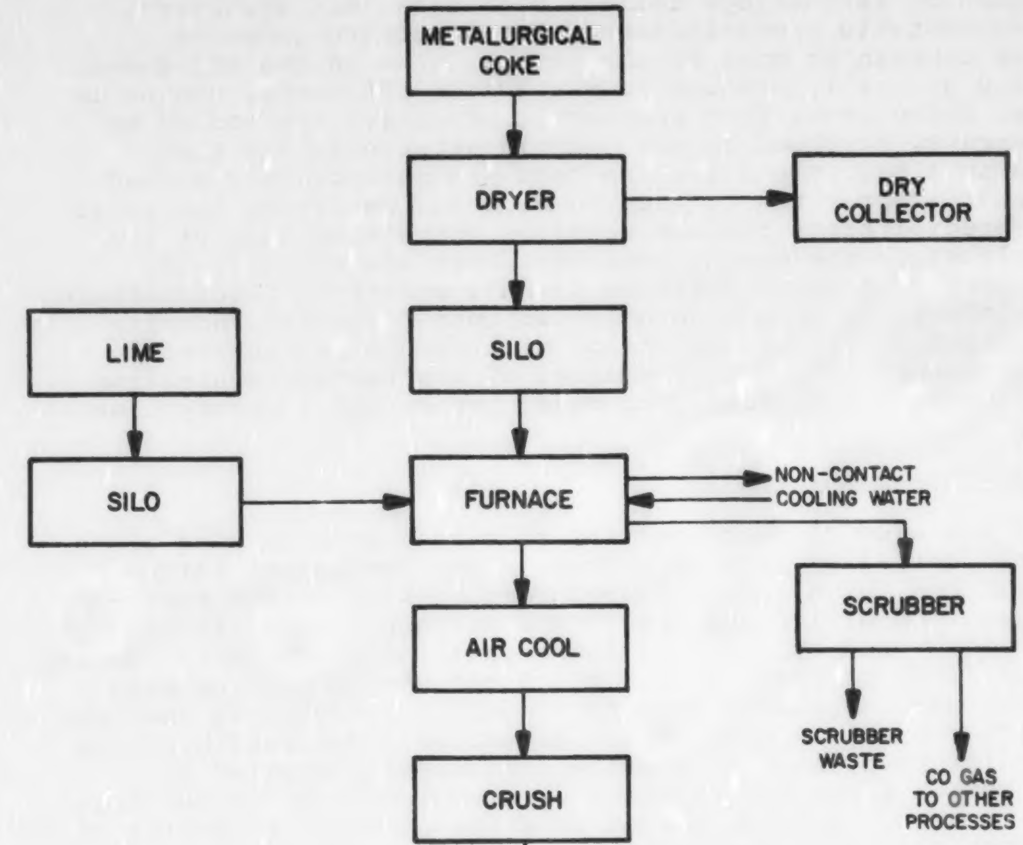

METALURGICAL COKE
DRYER
DRY COLLECTOR
LIME
SILO
SILO
FURNACE
NON-CONTACT COOLING WATER
SCRUBBER
SCRUBBER WASTE
CO GAS TO OTHER PROCESSES
AIR COOL
CRUSH
SCREEN
DRY COLLECTOR
PACKAGE
SHIP

FIGURE 8-20-3

COVERED FURNACE CALCIUM CARBIDE PROCESS FLOW DIAGRAM WITH WET AIR POLLUTION DEVICE

Electrolytic Manganese Products (F)

Manganese is produced by the electrolysis of an electrolyte extracted from manganese ore or manganese-bearing ferroalloy slag. A process flow diagram for the manufacture of electrolytic manganese is shown in Figure 8-20-4.

The process is essentially a four-step operation, namely, roasting the ore, leaching the ore, purifying the leach liquor, and electrolysis. The ground and roasted ore is leached with recycled anolyte from the electrolytic cell. Overall extraction of manganese from the roasted ore is 98-99 percent. The neutral leach liquor also contains iron, arsenic, copper, zinc, lead, nickel, cobalt and molybdenum, which must be removed before electrolysis. This is accomplished by treatment with hydrogen sulfide gas or ammonium sulfide and filtration of the liquor to remove the sulfide. The purified solution for electrolysis enters the cathode compartment, where managese is plated on the cathode. Manganese dioxide is prepared synthetically by electrolysis of manganese sulfate in a sulfuric acid solution. Wastewater streams from electrolytic manganese production contain T55, manganese, ammonia-nitrogen, and sulfate as the significant pollutants.

Electrolytic Chromium (G)

High-carbon ferrochromium produced in the electric furnace is the most readily available, cheapest, and one of the purest feedstocks of electrolytic chromium. A process flow diagram for the production of electrolytic chromium is shown in Figure 8-20-5.

Ferrochromium is fed to a leach tank and dissolved in a mixture of reduced anolyte, chromium alum liquor and makeup sulfuric acid. During the reaction, a large volume of hydrogen is released and a ventilating system, necessary to maintain hydrogen concentration below explosive limits, exhausts the gases to a scrubber. The slurry is then fed to a holding tank where cold liquor, coming from the ferrous amonium sulfate crystallization, is added to cool the batch. Undissolved solids are separated from the solution and this residue is washed with water and discarded. Ammonium sulfate is added to this solution and ferrous ammonium sulfate crystals then separated on a vacuum filter, dried, and sold for fertilizer. The filtrate is advanced to a conditioning tank, where the chromium is converted to the non-alum-forming modification by holding at elevated temperatures for several hours. The conditioned liquor is clarified and sent to the aging circuit. The crystal slurry is filtered and washed. The filtrate is pumped to the leach circuit and the washed chromium-alum crystals are dissolved in hot water to produce cell feed. The electrolytic cells are covered and are strongly ventilated to reduce the ambient hydrogen and hexavalent chromium concentrations in the cell room. Cathodes are withdrawn periodically from the cells and the plated metal is stripped,crushed, and washed with hot water to remove soluble salts. Wastewaters are characterized by significant concentrations of chromium, hexavalent chromium and calcium.

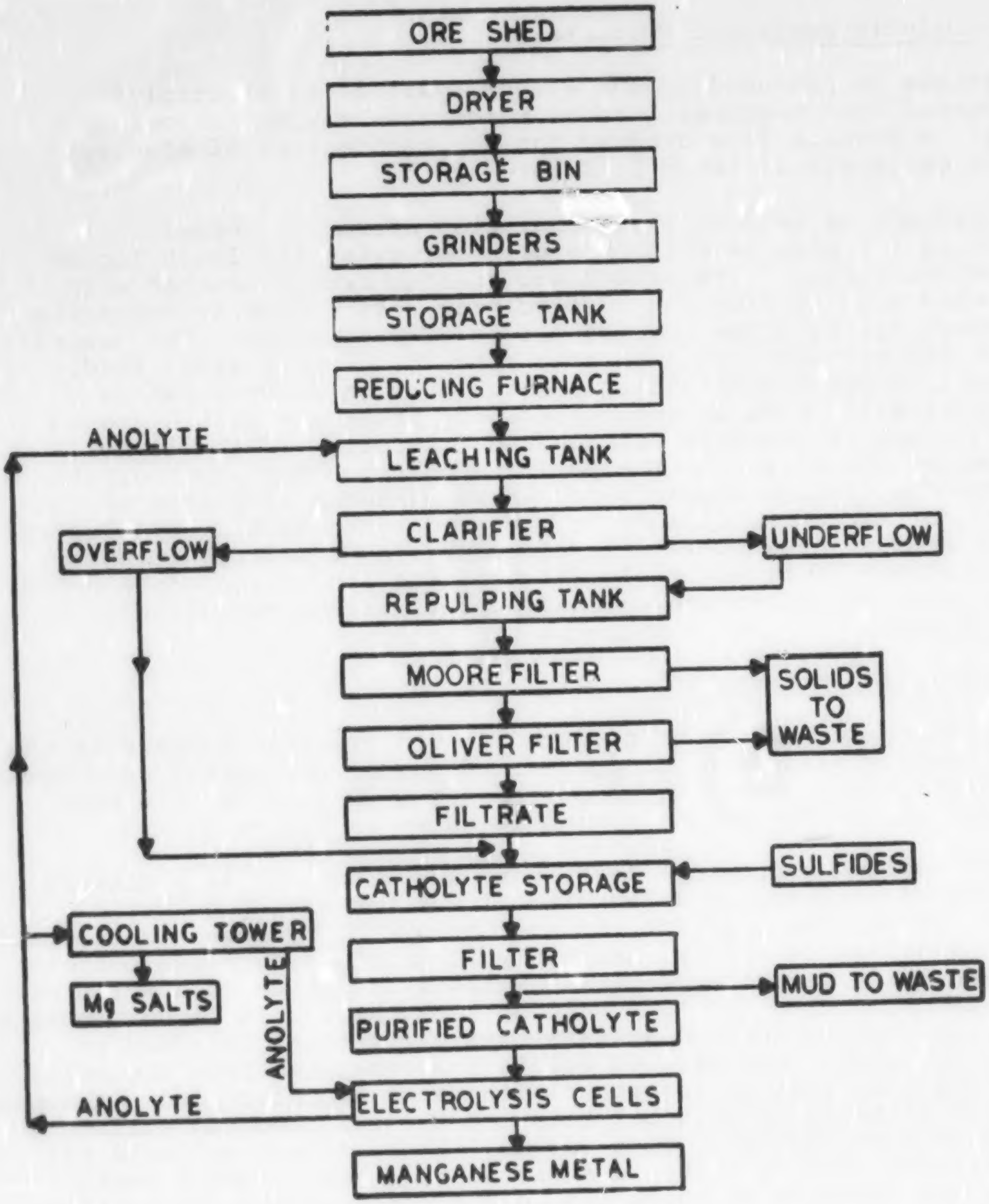

ORE SHED
DRYER
STORAGE BIN
GRINDERS
STORAGE TANK
REDUCING FURNACE
ANOLYTE
LEACHING TANK
CLARIFIER
OVERFLOW
UNDERFLOW
REPULPING TANK
MOORE FILTER
SOLIDS TO WASTE
OLIVER FILTER
FILTRATE
CATHOLYTE STORAGE
SULFIDES
COOLING TOWER
FILTER
Mg SALTS
MUD TO WASTE
ANOLYTE
PURIFIED CATHOLYTE
ANOLYTE
ELECTROLYSIS CELLS
MANGANESE METAL

FIGURE 8-20-4
ELECTROLYTIC MANGANESE FLOWSHEET

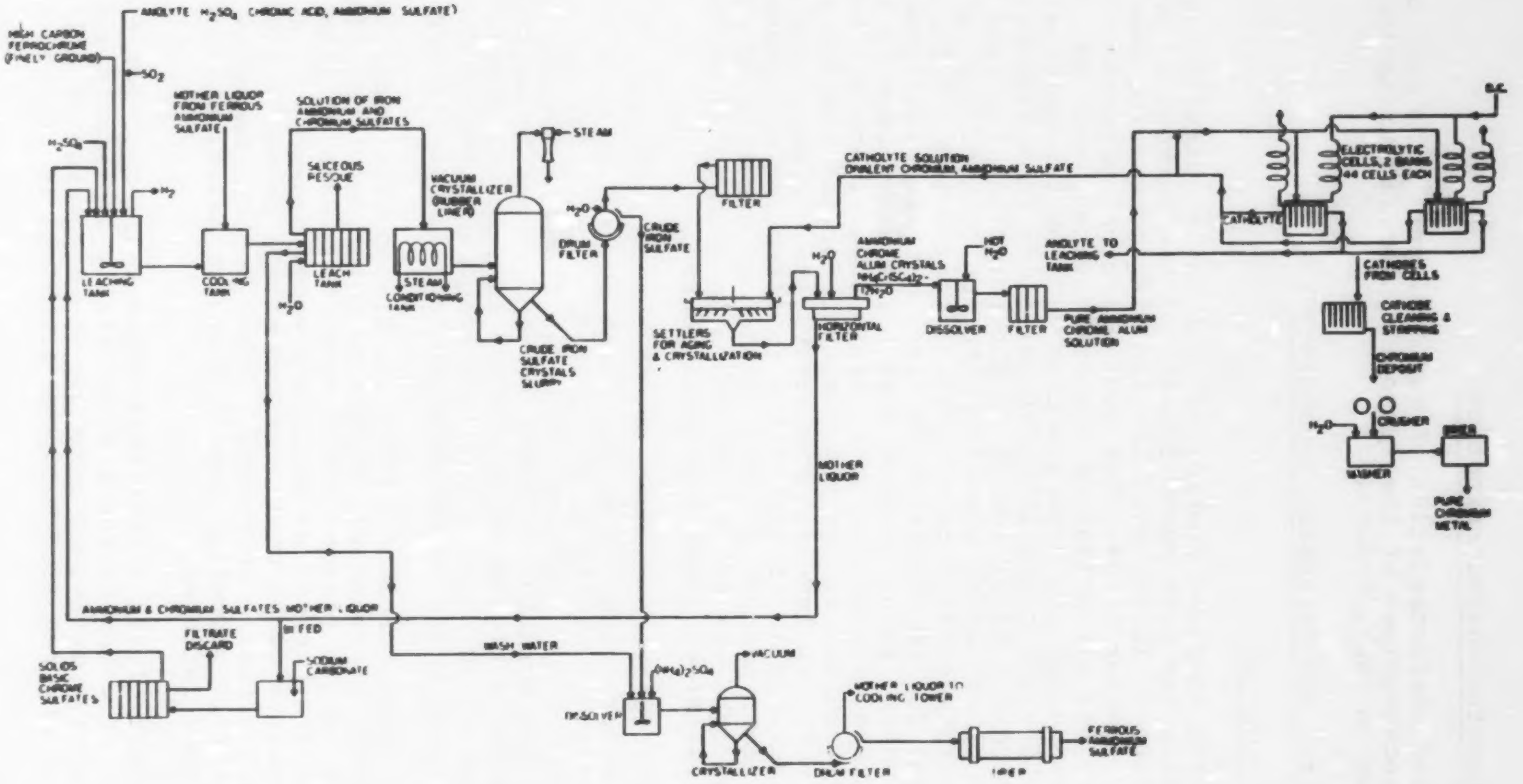

HIGH CARBON FERROCHROME (FINELY GROUND)
ANOLYTE H_2SO_4 (CHROMIC ACID, AMMONIUM SULFATE)
SO_2
H_2SO_4
H_2
LEACHING TANK
MOTHER LIQUOR FROM FERROUS AMMONIUM SULFATE
COOLING TANK
SOLUTION OF IRON AMMONIUM AND CHROMIUM SULFATES
SILICEOUS RESIDUE
LEACH TANK
H_2O
STEAM
CONDITIONING TANK
VACUUM CRYSTALLIZER (RUBBER LINED)
STEAM
CRUDE IRON SULFATE CRYSTALS SLURRY
H_2O
DRUM FILTER
CRUDE IRON SULFATE
FILTER
SETTLERS FOR AGING & CRYSTALLIZATION
CATHOLYTE SOLUTION DIVALENT CHROMIUM, AMMONIUM SULFATE
H_2O
HORIZONTAL FILTER
AMMONIUM CHROME ALUM CRYSTALS $NH_4Cr(SO_4)_2 \cdot 12H_2O$
HOT H_2O
DISSOLVER
FILTER
PURE AMMONIUM CHROME ALUM SOLUTION
ANOLYTE TO LEACHING TANK
CATHOLYTE
ELECTROLYTIC CELLS, 2 BANKS 44 CELLS EACH
D.C.
CATHODES FROM CELLS
CATHODE CLEANING & STRIPPING
CHROMIUM DEPOSIT
H_2O
CRUSHER
WASHER
PURE CHROMIUM METAL
MOTHER LIQUOR
AMMONIUM & CHROMIUM SULFATES MOTHER LIQUOR
FILTRATE DISCARD
BI FED
SODIUM CARBONATE
SOLIDS BASIC CHROME SULFATES
WASH WATER
$(NH_4)_2SO_4$
VACUUM
DISSOLVER
CRYSTALLIZER
MOTHER LIQUOR TO COOLING TOWER
DRUM FILTER
FERROUS AMMONIUM SULFATE

FIGURE 8-20-5
FLOW SHEET FOR ELECTROLYTIC CHROMIUM

4. Wastewater Characterization

Wastewater characteristics of raw effluents from each of the seven subcategories of the ferroalloy manufacturing industry are shown in Table 8-20-3.

5. Control and Treatment Technology

In-Plant Control

Significant in-plant control of both waste quantity and quality is possible for most subcategories of the ferroalloy manufacturing industry. In the smelting and slag processing segment (A, B, C), water is used for five principal purposes: Wet scrubbing for air pollution control devices, cooling, sanitary, slag processing, and drainage from slag or raw material storage. The quantity and composition of emissions from ferroalloy furnaces have a major impact on the potential for water pollution in those plants using wet air pollution control devices. Higher emission levels often occur after interruptions in furnace operations due to electrode failure, metallurgical problems, serious water leaks, furnace hearth failure, major taphole problems, or electrical system failure. Close supervision and maintenance are required to prevent frequent furnace shutdowns and control emission levels. Similarly, the choice of air pollution control devices is of importance in affecting wastewater volumes. Open furnaces produce greater volumes of gas than do covered furnaces. The use of dry baghouses on open furnaces can eliminate all wastewater effluent from this source.

Water recirculation in both the scrubber system and the furnace cooling water system is an important control measure in reducing the wastewater volumes to be treated. Makeup for the scrubber system can be obtained from blowdown from the cooling water system. The scrubber effluent can be treated to oxidize the cyanides and a flocculant aid added to improve sedimentation in the thickener to which all of the scrubber water is discharged. The thickener overflow can then be recycled to the scrubbers.

In the calcium carbide segment (D, E), cooling water, either once-through or recycled, should be relatively free of wastes. Any contaminants present would come from leaks or recycle build-ups which are handled as ancillary water blowdown. In either event, cooling waste contributions should be small and treatment should not normally be needed. Other control measures include containment of rainwater runoff from ore piles, and safeguards against pond failures.

In the electrolytic ferroalloys segment (F, G), recirculation and reuse of water is the most generally applicable and singly most effective method of reducing the discharge of pollutants. So long as any required blowdown discharge is treated to the

TABLE 8-20-3
FERROALLOY MANUFACTURING INDUSTRY

Raw Wastewater Characteristics

Parameter(mg/l)	Open Electric Furnace with Wet Air Pollution Control Devices A	Covered Electric Furnace & Other Smelting Operations with Wet Air Pollution Control Devices B	Slag Processing C	Covered Calcium Carbide Furnaces with Wet Air Pollution Control Devices D	Other Calcium Carbide Furnaces E	Electrolytic Manganese Products F	Electrolytic Chromium G
Flow Range(GPD)				112M - 148M	659M - 1648M	150M	210M
Flow Type	C	C	C	C	C	C	C
TSS (mg/l)	1460	1555	864	3750	-	2 - 900	290
TDS				302	-		
Total Chromium	4.76*	4.76*	2.04*				1764*
Hexavalent Chromium	0.32	0.32					
Manganese	613*	447*	54*			27*- 124*	52*
Total Cyanide		2.49*		27*	-		
Phenol		7.27					
Iron				14.2*	-		4492*
Silica				2.9	-		
Calcium				397	-		
Ammonia - N						87 - 94	1076*
Sulfate						180 - 688	
pH	7.2	6.0 - 9.0	6.2			2.7* - 7.3	2.9*

Note: *See Appendix 5 for parameters which may be inhibitory to biological systems.
M -Thousand C - Continuous

same effluent concentration as once-through water, the load reduction for each contaminant will be in direct proportion to the percentage of water recirculated. Water quality restrictions can generally be handled by using fresh makeup water at the points requiring high quality water.

Treatment Technology

The various wastewater treatment practices for each of the subcategories are summarized in Table 8-20-4.

TABLE 8-20-4
FERROALLOY MANUFACTURING INDUSTRY WASTEWATER TREATMENT PRACTICES REMOVAL EFFICIENCIES (PERCENT)

Pollutant & Method	Open Electric Furnace with Wet Air Pollution Control Devices A	Covered Electric & Other Smelting Operations with Wet Air Pollution Control Devices B	Slag Processing C	Covered Calcium Carbide Furnaces with Wet Air Pollution Control Devices D	Other Calcium Carbide Furnaces E	Electrolytic Manganese Products F	Electrolytic Chromium G
Suspended Solids							
1. Water Recirculation, lagoons, clarifier-Flocculators	98	98	97	98	-	97	97
2. Lagoons, clarifier-flocculators, sand filters and process water recirculation	99	99	98	99	-	99	99
Chromium							
1. Hexavalent chromium reduction, precipitation, sedimentation	89	89	76			90	90
Cyanide							
1. Alkaline chlorination		80		80	-		
Manganese							
1. Neutralization of acid salts, precipitation, and sedimentation	98	98	81			98	80
Phenol							
1. Breakpoint Chlorination, activated carbon		94					
Iron							
1. Neutralization, precipitation, and sedimentation				81		98	98
Calcium							
1. Water circulation, lagoons, clarifier-flocculators				92	-		
pH							
1. Neutralization	97	97	97	97	-	97	97

1. General Industry Description

Tanning is the process of converting animal hides into leather. The hides are unhaired, tanned by reacting with one or a combination of tanning agents, dyed and finished to produce a finished leather. Seventy-five percent of the industry's wastewaters are discharged to municipal sewer systems.

Establishments engaged in this industry are covered by Standard Industrial Classification(SIC)3111.

2. Industrial Categorization

A useful categorization for the purposes of raw waste characterization is given in Table 8-21-1.

3. Process Description

The subcategories in Table 8-21-1 include various combinations of four basic operations:

a. Beamhouse
b. Tanhouse
c. Retan, color, and fatliquor
d. Finishing

Discussion begins with a description of these four basic operations and follows with a definition of the subcategories based on these operations. Figure 8-21-1 shows a flow diagram for a typical cattlehide tannery.

Beamhouse

In the beamhouse,hides are processed in order to prepare them for the tanning operation. Hides that have been cured with salt or brine are received, stored, trimmed, and soaked to restore moisture and to remove salt. Wash waters contain dirt, salt, blood, manure and proteins, which are high in BOD, COD, dissolved and suspended solids.

Degreasing operations with either hot water and detergent or solvent are performed on pig and sheep skins. Much of the grease and solvent are recovered, but quantities of grease, BOD, COD and suspended solids enter the waste stream.

Fleshing, the removal of fatty tissue and meat from the hides, is accomplished on a fleshing machine, through the use of rotating blades. Cold water, necessary to keep the fat congealed, generates a fatty wastewater. Fleshings are recovered and sold to plants for rendering or for conversion to glue.

TABLE 8-21-1
LEATHER TANNING AND FINISHING

Subcategory	Designation
Hair Pulp Unhairing with Chrome Tanning and Finishing	A
Hair Save Unhairing with Chrome Tanning and Finishing	B
Hair Save Unhairing with Vegetable or Alum Tanning and Finishing	C
Finishing of Tanned Hides	D
Vegetable or Chrome Tanning of Unhaired Hides	E
Unhairing with Chrome Tanning and No Finishing	F

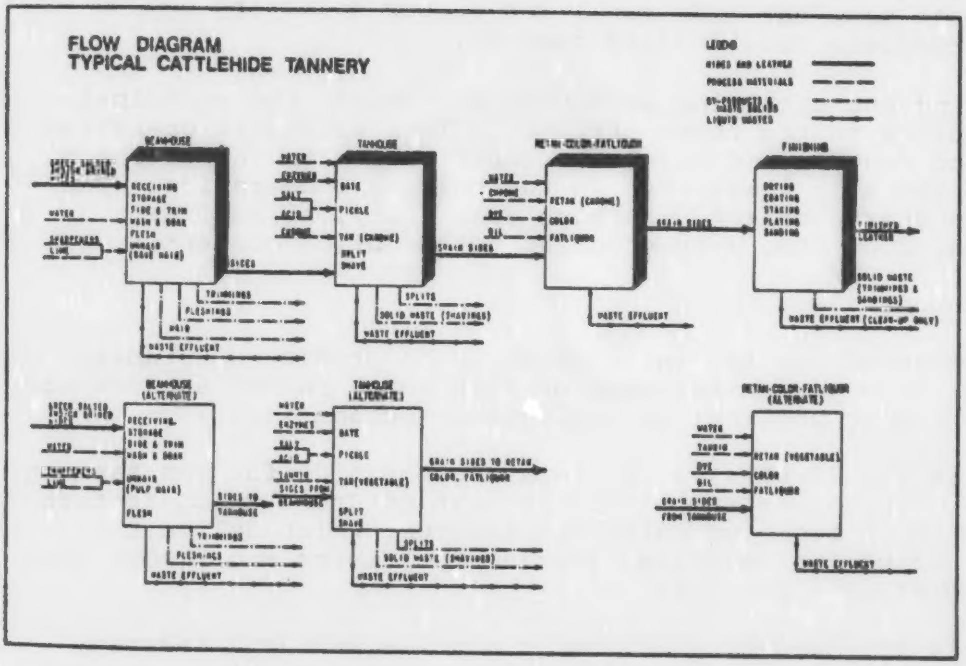

FLOW DIAGRAM
TYPICAL CATTLEHIDE TANNERY
LEGEND
HIDES AND LEATHER
PROCESS MATERIALS
BY-PRODUCTS & WASTE SOLIDS
LIQUID WASTES
BEAMHOUSE
GREEN SALTED, SWITCH DRIED HIDES
RECEIVING
STORAGE
SIDE & TRIM
WASH & SOAK
FLESH
UNHAIR (SAVE HAIR)
WATER
SHARPENERS LIME
SIDES
TRIMMINGS
FLESHINGS
HAIR
WASTE EFFLUENT
TANHOUSE
WATER
ENZYMES
SALT
ACID
CHROME
BATE
PICKLE
TAN (CHROME)
SPLIT
SHAVE
GRAIN SIDES
SPLITS
SOLID WASTE (SHAVINGS)
WASTE EFFLUENT
RETAN-COLOR-FATLIQUOR
WATER
CHROME
DYE
OIL
RETAN (CHROME)
COLOR
FATLIQUOR
GRAIN SIDES
WASTE EFFLUENT
FINISHING
DRYING
COATING
STAKING
PLATING
SANDING
FINISHED LEATHER
SOLID WASTE (TRIMMINGS & SANDINGS)
WASTE EFFLUENT (CLEAN-UP ONLY)
BEAMHOUSE (ALTERNATE)
GREEN SALTED, SWITCH DRIED HIDES
WATER
SHARPENERS LIME
RECEIVING
STORAGE
SIDE & TRIM
WASH & SOAK
UNHAIR (PULP HAIR)
FLESH
SIDES TO TANHOUSE
TRIMMINGS
FLESHINGS
WASTE EFFLUENT
TANHOUSE (ALTERNATE)
WATER
ENZYMES
SALT
ACID
TANNIC
SIDES FROM BEAMHOUSE
BATE
PICKLE
TAN (VEGETABLE)
SPLIT
SHAVE
GRAIN SIDES TO RETAN, COLOR, FATLIQUOR
SPLITS
SOLID WASTE (SHAVINGS)
WASTE EFFLUENT
RETAN-COLOR-FATLIQUOR (ALTERNATE)
WATER
TANNIC
DYE
OIL
GRAIN SIDES FROM TANHOUSE
RETAN (VEGETABLE)
COLOR
FATLIQUOR
WASTE EFFLUENT

FIGURE 8-21-1
Leather Tanning and Finishing

Beamhouse operations are classified according to one of two hair removal practices. Machine removal permits hair recovery and is practiced in a "save hair" beamhouse. The dissolving process is referred to as "pulping" and is practiced in a "pulp hair" beamhouse.

Prior to unhairing, the hides are slurried with lime and other additives, primarily sulfide sharpeners, to loosen the hair before its removal. Following unhairing the hides are sometimes relimed to make the hide swell for easier splitting and to assure complete hair follick removal.

The liming and unhairing processes are among the principal contributors to the waste effluent. In a save hair operation with good recovery of hair, the contribution to the effluent is substantially lower than in the pulp hair operation. The waste is characterized by a high alkalinity, pH,sulfide, nitrogen, BOD, COD, suspended and total solids content.

Tanhouse

The purpose of the tanning process is to produce a durable material from the animal skin or hide which is not subject to degradation by physical or biological mechanisms.

Bating is the first step in preparing the hide for the tanning process. The hides are placed in vats or drums which contain a solution of ammonium salts and enzymes, which delime the skins, reduce the swelling, peptize the fibers and remove protein degradation products.

Bating is followed by pickling in a brine and acid solution in order to condition the hide for receiving the tanning agent. Principal waste constituents are acid and salt.

Tanning is accomplished by reacting the hides with a tanning agent, usually chrome or vegetable tannins, although alum, metal salts and formaldehyde can be used. Waste effluents from the tanning process are substantial. Recycle and recovery of tanning agents are becoming more common. The spent chromium tanning solution is relatively low in BOD, COD, and suspended solids. On the other hand, vegetable tannin in the waste is a large source of both BOD and color.

Retan, Color, Fatliquor

These three operations are usually performed in one drum. Tanning solution is added to provide additional penetration into the hides(retan); synthetic or vegetable dyes are added to color the hides (color); oils are added to replace the natural oils of the skin that were lost in the tanning process (fatliquor). High strength, low volume discharges containing oil and color are generated.

Finishing

There are a number of finishing operations including drying, coating, staking and sanding which are principally dry processes. Pasting and washup operations generate a high strength low volume wastewater.

Table 8-21-2 shows the varying combinations of processes which determine the basis for subcategorization. Subcategory E includes the chrome tanning of unhaired and pickled sheep skins after removing the wool. There is generally no beamhouse process used for sheep or pig skins.

4. Wastewater Characteristics

Tables 8-21-3 and 8-21-4 contain raw wastewater characteristics for the industry. Most processes are batch operated, generating large fluctuations in wastewater strength and flow.

Sewerage systems are susceptible to damage from tannery wastes. An alkaline sulfur bearing waste when mixed with domestic or acidic waste will release hydrogen sulfide gas. Aerobic bacteria oxidize hydrogen sulfide to sulfuric acid which is corrosive to concrete and metal. Grease can coat sewer lines and act as an adhesive for particulate matter.

Aerobic biological treatment systems would possible be seriously inhibited by some tannery waste constituents. While normal average concentrations of lime and chromium salts may not damage the system, short term high concentrations could possibly be detrimental to biological activity. Experience with separate biological treatment of tannery wastewater has not indicated a serious problem with inhibition and treatment system upsets.

5. Control and Treatment Technology

Wide fluctuations in flow and strength can cause difficulties for the municipal treatment plant. Reductions in BOD, sulfides and chromium concentrations, as well as equalization of flow may be required to avert overloading biological units. Methods of reducing waste loads include:

a. Water conservation
b. Process solution reuse or recovery
c. Treatment to reduce a waste constituent

In-Plant Control

Water conservation measures in one tannery reduced water volumes by nearly 50%. These measures include reuse of process waters in the liming operations, screening and recirculating wash water, recycling vegetable tannin and evaporating the water and substituting hide processors (concrete mixers).

TABLE 8-21-2
LEATHER TANNING AND FINISHING
Principal Processes of Subcategories

Subcategory	Beamhouse	Tanning	Finishing
A	Hair Pulp	Chrome	Yes
B	Hair Save	Chrome	Yes
C	Hair Pulp or Save	Vegetable or Alum	Yes
D	None	None	Yes
E	None	Vegetable or Chrome	Yes
F	Hair Pulp or Save	Chrome	No

TABLE 8-21-3
LEATHER TANNING INDUSTRY

Raw Wastewater Characteristics

Parameter (mg/1)	Pulp-Chrome Finish A	Save-Chrome Finish B	Unhairing-Veg.-Finish C	Finish D	Veg. or Chrome E	Unhairing Chrome Tanning F
BOD	2000*	1100*	1400*	2000*	1100*	4000*
TSS	2500	2300	2700	2400	1400	4000
pH						9-11*
Oil & Grease	350*	700*	650*	400*	400*	250*
COD	5000*	2200*	5000*	1500*	2700*	8000*
Total Nitrogen	350	200	200	200	100	600
Sulfide	150*	15	25	100*	72*	150*
Chromium	80*	80*	4*	130*	20*	160*
Alkalinity	2000	1150	1300	2000	1100	1500

Note: *See Appendix 5 for parameters which may be inhibitory to biological systems

TABLE 8-21-4
LEATHER TANNING INDUSTRY
Raw Wastewater Characteristics - Production Based Data

Parameter (kg/kkg)	Pulp-Chrome Finish A	Save-Chrome Finish B	Unhairing Veg-Finish C	Finish D	Veg or Chrome E	Unhairing Chrome Tan F
Flow Range (1/kkg)	7M/156M	1M/189M	7M/106M	3M/33M	6M/205M	14M/56M
Flow Type	B	B	B	B	B	B
BOD	5/270	20/140	8/130	7/70	10/140	30/160
TSS	7/600	30/350	20/450	7/130	3/870	40/190
Oil & Grease	.1/70	.7/110	.1/160	2.2/19	.6/46	1/19
COD	10/600	90/220	25/700	5.5/65	11/270	50/160
Total Nitrogen	3/44	3.5/25	1/25	1/7	.6/30	14/18
Sulfide	.1/46	.1/3	.1/4	2	4/5	2/6.5
Chromium	.1/19	.3/12	.2/.6	.4/5	.1/2.1	3.8/6
Alkalinity	.5/300	60/90	4/140	40	6.5/180	35/55

Note: M - thousand
B - batch process
kg/kkg - kilogram pollutant/1000 kilograms of product produced (lower limit/upper limit)
1/kkg - liters of wastewater/1000 kilograms of product

Reuse and recovery of tanning solutions, unhairing solutions, pickle liquor, retan liquor, and pasting frame water, have been successfully accomplished, with significant reductions in waste load.

Treatment Technology

Sulfides in the beamhouse waste constitute a potential problem in subsequent handling. Sulfides are satisfactorily removed by means of oxidation by air, chemical or catalytic methods.

Chromium is used exclusively in the trivalent form, which can be precipitated and clarified with proper pH adjustment and suitable equipment. However, some tanneries buy hexavalent chrome and convert this to the trivalent from. Spills from the storage of hexavalent chrome must be kept separate from other wastes since it must be reduced to the trivalent state before it can be removed by precipitation.

Other preliminary treatment operations consist of one or a combination of the following: screening, equalization, sedimentation, coagulation and sedimentation and secondary treatment. With adequate pretreatment,tannery wastes are acceptable to municipal treatment systems.

Table 8-21-5 contains removal efficiencies for some treatment processes.

TABLE 8-21-5

Leather and Tanning Industry Treatment Practices

Removal Efficiencies

Pollutant and Method	Percent Removal
BOD	
1. Sedimentation	30-60
2. Coagulation and Sedimentation	70-85
3. Biological treatment	70-98
TSS	
1. Sedimentation	40-70
2. Coagulation and Sedimentation	80-95
3. Biological treatment	70-98
Grease	
1. Sedimentation	50-90
2. Coagulation and Sedimentation	50-90
Chromium	
1. Sedimentation	50-90
2. Coagulation and Sedimentation	90-98

1. General Industry Description

The Insulation Fiberglass segment of the glass manufacturing industry is that part of the industry in which molten glass is made into continuously fiberized and chemically bonded, wool-like material. Several air pollution abatement methods practiced by this industry produce large volumes of wastewater. These discharges contain moderate amounts of phenol, dissolved solids, COD, and considerable amounts of suspended solids.

The flat glass industry involves the manufacturing of primary flat glass by melting sand with other inorganic raw materials at high temperatures, forming the molten mass into the basic sheet by various methods and fabricating it into flat glass products. Waters from cooling, washing and polishing operations are the principal sources of waste discharges containing heat, suspended solids, oils and occasionally phosphates. Water recycling is practiced throughout the industry to reduce the large volume of dilute waste. Establishments engaged in this industry are covered by Standard Industrial Classification (SIC) 3211, 3231, 3296.

2. Industrial Categorization

The industry has been categorized along process lines and subcategorized according to similarities in wastes as follows:

Category	Subcategory	Designation
Insulation Fiberglass	Insulation Fiberglass	A
Flat Glass	Sheet Glass	B
	Rolled Glass	C
	Plate Glass	D
	Float Glass	E
Automotive Glass	Tempered	F
	Laminated	G

3. Process Description

Insulation Fiberglass (A)

Glass fiber has the ability to form low thermal conductivity webs which retard, inexpensively, the transfer of heat. The manufacture of the insulation itself is a simple, large-scale process which has three distinct steps:

a. Glass melting

b. Glass spinning or fiberizing

c. Insulation binding and forming

Glass melting is performed in either a semi-batch Multiple Remelt Furnace or in the more preferred Direct Melt Furnace which melts the ingredients and feeds molten glass to the fiberizers in one continuous operation.

Spinning or fiberizing molten glass is performed by either a Flame Attenuation or a Rotary Spinning process. In the former, molten glass from the furnace falls through fine holes bored in platinum bushings and comes out as relatively thick fibers which are drawn or attenuated into thin fibers by passing them through a stream of high velocity hot gas. In the more productive rotary process a single stream of molten glass is fed into a spinning platinum basket containing a large number of small holes in its wall and the molten glass is forced through the holes by centrifugal force, thereby forming the fibers. These fibers, too, are drawn or attenuated by high velocity, hot gases and fall as a mass onto a moving conveyor.

The fibers are sprayed with a phenolic water soluble binder or glue. This binder, a complex mixture of thermosetting organic resins, oils, dyes, and chemical additives is a major source of pollution from the plant. The glass fiber mat is conveyed through the appropriate curing and cooling ovens on a conveyor to the packaging department. During spraying the conveyors are exposed to and collect deposits of the resinous binder which are removed by hot caustic baths or by pressurized water sprays. The latter is preferred because the sprayed water is amenable to treatment and recirculation while spent caustic must be dumped.

Insulation fiberglass plants experience both air particulate and odor problems. Particulate emissions are found in the exhaust gases of the glass furnace, forming area, and curing and cooling ovens. The principal source of odors is volatilized phenols. Several methods, involving both wet and dry processes, are being developed in an effort to reduce the air emissions.

FLAT GLASS

Primary flat glass operations of batching, melting, forming and cutting are basic to all glass manufacturing. In batching, silica sand, soda ash, limestone, dolomite and cullet (broken waste glass) are mixed. The mix is fed to a high temperature melt tank that produces molten glass. Non-contact cooling waters generate thermal discharge. The method by which the glass is removed from the melt tank is the distinguishing factor among subcategories B-G.

Sheet Glass (B)

In Sheet Glass (B) molten glass is drawn vertically from the melt tank as a ribbon. The thickness of this ribbon of glass is inversely proportional to the drawing speed. Wastewater is produced in the fabricating operations on the produced sheet. No water is used in the forming of sheet glass or in the first cutting. If the glass is to be further fabricated, water may be used.

Rolled Glass (C)

Rolled glass is flat plate manufactured with decorative and diffuse textures and can include safety wire inclusions. Rolled glass is produced by gravity feeding molten glass through texturized rolls which impart the desired surface, or by inserting wire mesh between two ribbons of hot and soft glass which bond together when they touch. Wastewaters are limited to thermal discharges from cooling waters.

Plate Glass (D)

Plate glass manufacturing is the production of high quality thick glass sheet. Rough glass is produced by gravity feeding molten glass between water cooled forming rolls. Rough glass sheet is transformed to a quality glass finished product by grinding and polishing with slurries of progressively finer abrasives. The polishing residues are removed by a series of washes and rinses. Large quantities of wastewater containing suspended solids as well as large quantities of cooling water are generated.

Float Glass (E)

The manufacturing of flat glass by the float process is more efficient and results in the discharge of much less wastewater than the Plate Glass (D) process. In the float process, molten glass is poured onto a molten tin surface where heat and the force of gravity combine to form a high quality plate glass that requires no grinding and polishing. The underside of the glass is sprayed with sulfur dioxide after forming to provide a protective coating of sodium sulfate. This coating is subsequently washed off before further fabricating. The elimination of the grinding and polishing process, characteristic of plate glass manufacturing, is the float process' main advantage, and results in significantly reduced wastewater volumes. Recycling is practiced in the washing procedure with occasional blowdowns to regulate dissolved solids build up. However, glass for mirror manufacture has a higher quality rinse water requirement precluding the use of recycled water.

FABRICATED AUTOMOTIVE GLASS

Tempered Glass (F)

Solid tempered automotive fabrication is the fabrication from glass blanks of automobile back and side windows by a series of operations in which flat glass is cut, drilled, ground smooth, bent and tempered in preparation for installation. The grinding and washing operations produce water borne pollutants. An oil-water emulsion used in the grinding process (as a coolant and to remove glass particles) is the main source of oil and suspended solids. Washing to cleanse the glass of residual coolant and particles prior to tempering is another source of wastewater. Both wastewaters are generally recycled. Cooling water is required for tempering and quenching but the heat rejected here is relatively low.

Laminated Glass (G)

Windshield fabrication is the manufacturing of laminated windshields from glass blanks and vinyl plastic. Two layers of glass which have been cut and bent to proper size and curvature are bonded with an inner layer of vinyl plastic. Bending to appropriate curvature is accomplished in a heating lehr where mating panels are shaped as a pair. The cementing is done in oil (usually) or air (more recently) autoclaves in which adherence between the three layers is induced by high pressure and temperature. Wastes are produced by the seaming (rough grinding of sharp edges) and frequent washings that are necessary to assure cleanliness of all glass and plastic surfaces before bending and laminating. Blowdown from concentrated recycled streams contains oils, suspended and dissolved solids, and some detergent. Cooling waters generate thermal discharges.

4. Wastewater Characterization

Sources of wastewater include cooling operations, equipment cleaning, air pollution scrubbers, grinding and washing operations, boiler blowdown and water treatment sludges. Table 8-22-1 contains wastewater characteristics for the industry.

5. Control and Treatment Technology

In-Plant Control

The industry practices extensive recycling and reuse techniques in order to reduce wastewater volumes. The following modifications can reduce water use:

Replace caustic baths with pressurized water sprays to clean conveyors of fiber and resin.

Use water sprays with higher pressure to minimize water consumption.

Reuse of chain wash water after suitable treatment.

Dispose of high dissolved solids blowdown in overspray and binder dilution water.

Incorporate hood wash and miscellaneous process waters in the chain wash system.

Recirculate cullet cooling water with blowdown to the chain wash recirculation system.

In the windshield laminating process oil contamination can be reduced to a trace by converting the process to air autoclaves from existing oil units.

TABLE 8-22-1
GLASS MANUFACTURING

RAW WASTEWATER CHARACTERISTICS

Parameters (mg/1)	Fiberglass A	Sheet B	Rolled C	Plate D	Float E	Tempered F	Laminated G
BOD	156 - 7800*	NO DISCHARGE	NO DISCHARGE		2	15	33
COD	3290-43,000*			100	15	25	1700*
TDS				175	100	100	
Suspended Solids	200-40,000			15,000	15	100	25
Oil and Grease	7.5 - 140*			trace	5	13	1700*
Phenols	4 - 700						
Ammonia	.6 - 4.83						
Total Phosphorus							6
pH	9.0			9.0	8	7	7-8
Color	Yellow, brown						
Turbidity (JTU)	55 - 200						

* See Appendix 5 for parameters which may be inhibitory to biological systems.

Treatment Technology

The large volumes of solids-laden wastewater are normally treated by lagooning with polyelectrolyte added to increase settling. The lagoon effluent can be recycled back to the grinding and polishing steps. The quality of this effluent can be improved by using two-stage lagoons and/or sand filters. Oils can be removed by filtering through diatomaceous earth filters. Table 8-22-2 contains typical removals that can be expected from various wastewater treatment practices.

TABLE 8-22-2

WASTEWATER TREATMENT PRACTICES

GLASS MANUFACTURING

	Subcategories (% Removal)				
Pollutant and Method	Fiber Glass	Plate Glass	Float Glass	Solid Tempered Automotive	Windshield Fabrication
Suspended Solids					
Settling Lagoon-plus polyelectrolyte	-	99.6	-	-	-
Coagulation and Sedimentation	-	99.8	-	75	-
Sand Filtration	-	99.9	-	-	-
Diatomaceous Earth Filtration	-	-	66	95	80
Biological Treatment	97	-	-	-	-
Phenol					
Bioconversion	99.6	-	-	-	-
Oil					
Settling Lagoon	-	90	-	-	-
Diatomaceous Earth Filtration	-	-	66	62	99.7
API Separation	-	-	-	-	98*
Air Flotation	-	-	-	-	98
BOD					
Diatomaceous Earth Filtration	-	-	-	33	-
Biological Treatment	98.5	-	-	-	-
COD					
Settling Lagoon	-	90	-	-	-
Diatomaceous Earth Filtration	-	-	-	33	-
API Separation	-	-	-	-	98*
Biological Treatment	95	-	-	-	-

* Assumes process has replaced detergent wash with hot water rinse

1. General Industry Description

Asbestos is a group name that refers to several serpentine minerals having different chemical compositions,but similar characteristics. The most widely used variety is chrysotile. As a natural mineral fiber, asbestos is strong, flexible, and highly resistent to breakdown under adverse conditions. One or more of these properties are exploited in numerous manufactured products by combining asbestos with other materials such as binders, fillers, and additives for extensive applications. Principal product categories are asbestos-cement, floor tile, paper and felts, friction products, textiles, sprayed insulation, and packing and gaskets.

The increased concern over exposure to asbestos fibers in the air is primarily responsible for the gradual conversion of dry processes into wet processes in the industry. This trend is expected to continue in the future.

The asbestos manufacturing industrial category has the following Standard Industrial Classification (SIC) numbers: 3292, 3293 and 2661.

2. Industrial Categorization

The asbestos manufacturing industry is broadly subdivided into two main categories: the building, construction, and paper segment, and the textile, friction materials and sealing devices segment. For the purposes of raw waste characterization and delineation of pretreatment information, the industry is further subdivided into 11 subcategories, as shown below. Process effluents from the building, construction, and paper segment of the industry constitute the predominant source of wastewaters in this industrial category.

Main Category	Subcategory	Designation
1. Building, Construction, and Paper	Asbestos-Cement Pipe	(A)
	Asbestos-Cement Sheet	(B)
	Asbestos Paper (Starch Binder)	(C)
	Asbestos Paper (Elastomeric Binder)	(D)
	Asbestos Millboard	(E)
	Asbestos Roofing Products	(F)
	Asbestos Floor Tile	(G)
2. Textiles, Friction Materials, and Sealing Devices	Coating, or Finishing, of Asbestos Textiles	(H)
	Solvent Recovery	(I)
	Vapor Absorption	(J)
	Wet Dust Collection	(K)

3. Process Description

General

With the exception of roofing and floor tile manufacture, there is a basic similarity in the methods of producing the various asbestos products. The asbestos fibers and other raw materials are first slurried with water and then formed into single or multi-layered sheets as most of the water is removed. The manufacturing process always incorporates the use of save-alls (settling tanks of various shapes) through which the process waste waters are usually routed. Water and solids are recovered and reused from the save-all, and excess overflow and underflow constitute the process waste streams. In all of these product categories, water serves both as an ingredient and a means of conveying the raw materials to and through the forming steps.

Asbestos-Cement Products (A, B)

The largest single use category of asbestos fiber is the manufacture of asbestos-cement products. The pipe segment is the largest component in this product category. Asbestos-cement products contain from 10 to 70 percent asbestos by weight, usually of the chrysotile variety. Portland cement content varies from 25 to 70 percent. The remaining raw material, from 5 to 35 percent, is finely ground silica.

Asbestos-cement products are manufactured by the dry process, the wet process, or the wet mechanical process. In the dry process, which is suited to the manufacture of shingles or other sheet products (B), a uniform thickness of dry materials is distributed onto a conveyor belt, sprayed with water, and then compressed against rolls to the desired thickness and density. The major source of process waste water is the water used to spray clean the empty belt as it returns. The wet process produces dense sheets, either flat or corrugated, by introducing a slurry into a mold chamber and then compressing the mixture to force out excess water. A settling and hardening period precedes the curing process. The grinding operation used to finish the sheet surface produces a large quantity of dust which may be discharged with the process wastewaters. The wet mechanical process, which is also used for asbestos-cement pipe manufacture (A), utilizes willowed asbestos fiber which is conveyed to a dry mixer where it is blended with the cement, silica, and filler solids. The mixture is transferred to a wet mixer or beater, and underflow solids and water from the save-all are added to form a slurry which is pumped to cylinder vats for deposition onto horizontal screen cylinders. The resulting layer from each cylinder, usually from 0.02 to .10 inch in thickness, is transferred to an endless belt conveyor for further processing. Flow diagrams for the wet mechanical process for pipe manufacture and the dry process for sheet manufacture are shown in Figure 8-23-1. Asbestos-cement plants recycle the majority of their water as a means of recovering all usable solids. The save-all overflows may be discharged from the plant as effluents or treated and returned to the plant for whatever use its quality justifies. This includes water for saws, vacuum pump seals, cooling, hydrotesting, or make-up water for plant startup.

Asbestos Paper (C, D)

Asbestos paper is manufactured on machines of the Fourdrinier and cylinder types which are similar to those which produce cellulose paper. A mixing operation combines the asbestos fibers with the binders and other minor ingredients. A pulp beater or hollander mixes the fibers and binder with water into a stock which is diluted to as little as one-half percent fiber in the discharge chest. The discharge chest deposits a thin, uniform layer of stock onto an endless moving wire screen. A major portion of the water is drawn by suction boxes or rolls adjacent to the sheet of paper.

The sheet is then transferred to an endless moving belt and pressed to bring the paper to about 60 percent dryness. This is followed by calendering, to produce a smooth surface, and winding of the paper onto a spindle. The manufacturing process is shown in Figure 8-23-1. The majority of the water in a paper plant serves as an ingredient carrier and continually recirculates in a loop through the machine and the save-all. Occasionally, the solids from the save-all must be discharged from the plant due to a product change, rapid setup of the binder, or a plant shutdown.

Asbestos Millboard (E)

Asbestos millboard is produced on small cylinder-type machines similar to those used for making asbestos-cement pipe (A). The machines are equipped with one or two cylinder screens, conveying felt, pressure rolls, and a cylinder mold. After mixing and stirring, the slurry is transferred to a stock chest where it is diluted and pumped to the cylinder vats with large screens. The slurry flows through the screens, depositing a mat of fiber on the cylinder surface before flowing out through the ends of the cylinder. The mat is transferred to a carrier belt. Pressure rolls then remove water from the mat as it is wound onto the cylinder mold. Finished millboard usually contains 5 to 6 percent water. Most of the water in the manufacturing process serves as an ingredient carrier and continually circulates in a loop through the machine and the save-all. Excess overflow water must be discharged from the plant.

Asbestos Roofing (F)

Figure 8-23-1 shows the process flow diagram for asbestos roofing manufacture. Asbestos paper is pulled through a bath of hot coal tar or asphalt. After saturation, the paper passes over a series of hot rollers to set the coal tar or asphalt in the paper. After passing over cooling rollers, the roll of roofing is coated with various materials to prevent adhesion between layers. The roofing is finally air dried, rolled up, and packaged for marketing. Water is used in two ways. It is converted to steam to heat the saturating baths and hot rollers and for cooling the hot paper after it has been saturated. The only process wastewater is that originating in the spray cooling and, in many cases, this contaminated contact water is discharged with the clean non-contact cooling water.

Asbestos Floor Tile (G)

The tile manufacturing process involves several steps: ingredient weighing, mixing, heating, decoration, calendering, cooling, waxing, stamping, inspecting, and packaging. The ingredients are weighed and mixed dry. Liquid constituents, if required, are then added and thoroughly blended into the batch. After mixing, the batch is heated to about 150°C and fed into a mill where it is joined with the remainder of a previous batch for continuous processing through the rest of the manufacturing operation. Water serves only as a heat transfer fluid. Non-contact cooling water remains clean and can be reused continually if cooling towers or water chillers are available to remove the heat picked up from the hot tile. Leakages from various sources collect dirt, oil, grease, wax, ink, glue, and other contaminants.

Textiles (H), Solvent Recovery (I), Vapor Absorption (J), and Wet Dust Collection (K)

The products covered by the above four subcategories can be grouped into three types: Asbestos textile products, friction materials, and asbestos-containing gaskets, packings, and sealing devices. In most plants in these subcategories, water is not used in the manufacturing processes. However, process-related wastewaters are generated in a few plants by manufacturing operations or by air pollution control equipment. The basic manufacturing processes and the origin and nature of wastewaters for each of the three product types are outlined below. A process flow diagram for the manufacture of various asbestos textile products is shown in Figure 8-23-2. Asbestos fibers are received by railcar in 100-pound bags. The fibers are cleaned over vibrating screens or trommel screens. After preparation, the fibers are mixed and blended. The fibers are then arranged by thousands of needle-pointed wires which cover the cylinders of a carding machine. The resulting continuous

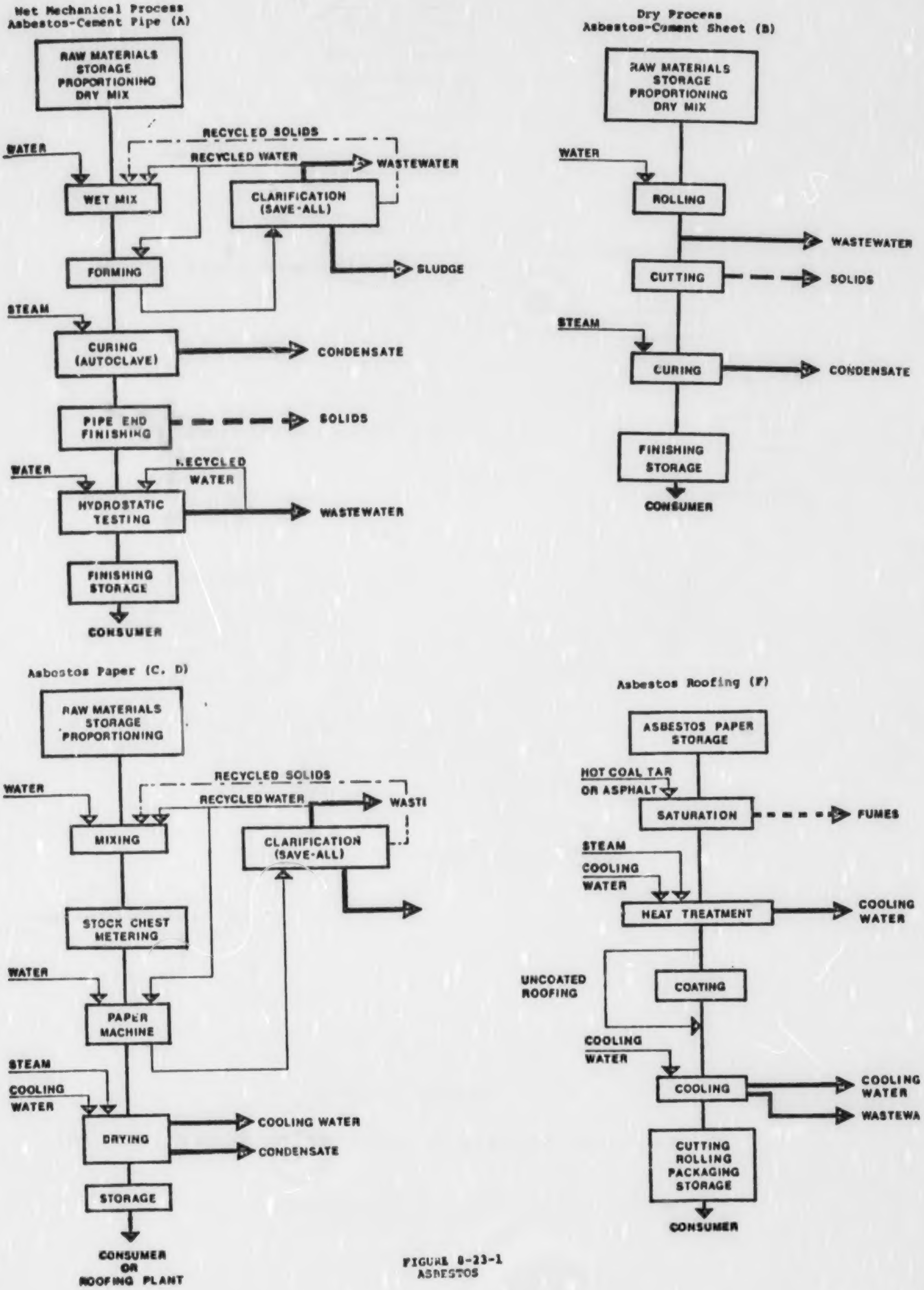

Wet Mechanical Process
Asbestos-Cement Pipe (A)
RAW MATERIALS STORAGE PROPORTIONING DRY MIX
WATER
RECYCLED SOLIDS
RECYCLED WATER
WASTEWATER
WET MIX
CLARIFICATION (SAVE-ALL)
FORMING
SLUDGE
STEAM
CURING (AUTOCLAVE)
CONDENSATE
PIPE END FINISHING
SOLIDS
WATER
RECYCLED WATER
HYDROSTATIC TESTING
WASTEWATER
FINISHING STORAGE
CONSUMER
Dry Process
Asbestos-Cement Sheet (B)
RAW MATERIALS STORAGE PROPORTIONING DRY MIX
WATER
ROLLING
WASTEWATER
CUTTING
SOLIDS
STEAM
CURING
CONDENSATE
FINISHING STORAGE
CONSUMER
Asbestos Paper (C, D)
RAW MATERIALS STORAGE PROPORTIONING
RECYCLED SOLIDS
WATER
RECYCLED WATER
WASTE
MIXING
CLARIFICATION (SAVE-ALL)
STOCK CHEST METERING
WATER
PAPER MACHINE
STEAM
COOLING WATER
DRYING
COOLING WATER
CONDENSATE
STORAGE
CONSUMER OR ROOFING PLANT
Asbestos Roofing (F)
ASBESTOS PAPER STORAGE
HOT COAL TAR OR ASPHALT
SATURATION
FUMES
STEAM
COOLING WATER
HEAT TREATMENT
COOLING WATER
UNCOATED ROOFING
COATING
COOLING WATER
COOLING
COOLING WATER
WASTEWA
CUTTING ROLLING PACKAGING STORAGE
CONSUMER

FIGURE 8-23-1
ASBESTOS

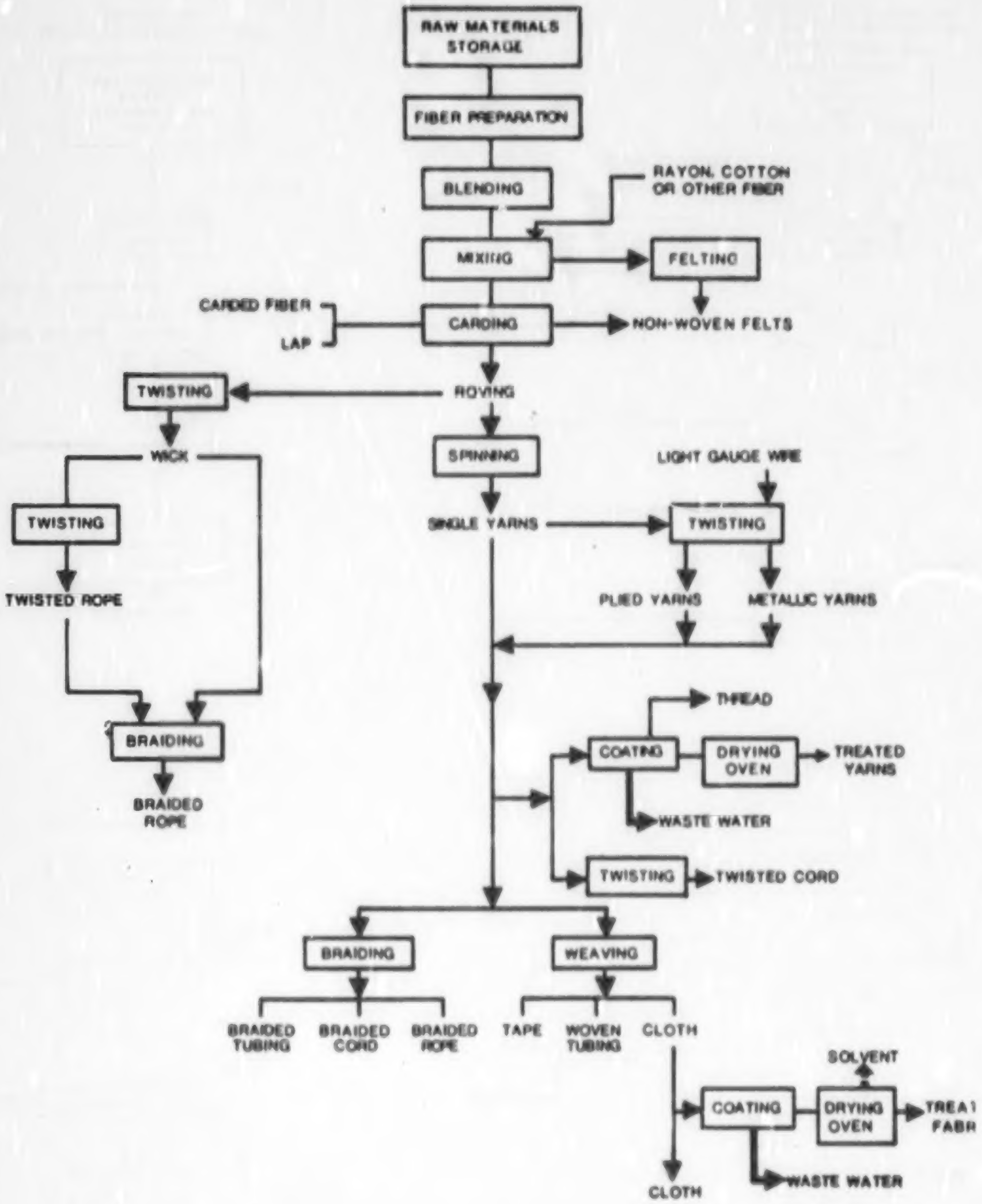

RAW MATERIALS STORAGE
FIBER PREPARATION
BLENDING
RAYON, COTTON OR OTHER FIBER
MIXING
FELTING
CARDED FIBER
LAP
CARDING
NON-WOVEN FELTS
TWISTING
ROVING
WICK
SPINNING
LIGHT GAUGE WIRE
TWISTING
SINGLE YARNS
TWISTING
TWISTED ROPE
PLIED YARNS
METALLIC YARNS
THREAD
BRAIDING
COATING
DRYING OVEN
TREATED YARNS
BRAIDED ROPE
WASTE WATER
TWISTING
TWISTED CORD
BRAIDING
WEAVING
BRAIDED TUBING
BRAIDED CORD
BRAIDED ROPE
TAPE
WOVEN TUBING
CLOTH
SOLVENT
COATING
DRYING OVEN
TREA
FABR
CLOTH
WASTE WATER

Figure 8-23-2

Asbestos Textile Manufacturing Operations (H) mat of material is divided into strips, or slivers, and mechanically compressed between oscillating surfaces into untwisted strands which are then wound on spools to form the roving. Roving is the asbestos textile product from which asbestos yarn is produced. Asbestos twine or cord is produced by twisting together two or more yarns on a spinning frame. Braided products are made by a series of yarn-carrying spindles, half traveling in one direction and half in the opposite direction to plait the yarn together and form the braided product. Asbestos yarn or cloth may be coated for fabrication into friction materials and special products. Water is not normally used in an asbestos textile manufacturing plant. Two exceptions are the addition of moisture during weaving or braiding and the coating operation. Wastewater is generated in the latter process.

Friction materials may be further classified into the molded products and woven products. Water is not used in the manufacturing processes. Wastewaters are generated in a few friction material plants in the solvent recovery operations and in the wet dust collection equipment. Similarly, water is not used in the manufacture of gaskets, packings, and sealing devices. The manufacture of sheet gasket material may involve cooling and solvent recovery operations, in which case process-related wastewaters are generated.

4. Wastewater Characterization

Wastewater characteristics of process effluents from each of the 11 subcategories of the asbestos manufacturing industry are shown in Table 8-23-1.

5. Control and Treatment Technology

In-Plant Control

Significant in-plant control of both waste quantity and quality is possible for most subcategories of the asbestos manufacturing industry. Important control measures include the proper storage of raw materials, segregation of wastewaters, good housekeeping practices, and water conservation. Raw materials should be stored indoors and kept dry. Sanitary wastes should be disposed of separately from process wastes. In plants where non-process wastes are combined with manufacturing wastes, a careful evaluation should be made to determine if some or all of these wastes could be segregated and recirculated. Fresh water should be used first for pump seals, steam generation, showers, and similar uses that cannot tolerate high contaminant levels. The discharges from these uses should then go into the manufacturing process as make-up water and elsewhere where water quality is less critical. In line with water use practices, evaluation of the benefits of increased save-all capacity should be made at some plants. This would provide more in-plant water storage, permit greater operating flexibility, and reduce the level of pollutant constituents in the raw wastewaters discharged from the plant.

TABLE 8-23-1
ASBESTOS MANUFACTURING INDUSTRY
RAW WASTE CHARACTERIZATION

Parameter (mg/l)	Asbestos-Cement Pipe A	Asbestos-Cement Sheet B	Asbestos-Paper (Starch Binder) C	Asbestos-Paper (Elastomeric Binder) D	Asbestos Millboard E	Asbestos Roofing Products F	Asbestos Floor Tile G	Coating, or Finishing of Asbestos Textiles H	Solvent Recovery I	Vapor Absorption J	Wet Dust Collection K
Flow Range (Gal. per day)	20K-500K	70K-540K	130K-1.3M	130K-1.3M	80K-600K	375K	10K-180K	200	10K	60K	50K-150K
Flow Type	B	B	C	C	B	B	B	B	C	B	B
BOD_5 (mg/l)	2	2	110	110	5	6-37	15		1125*		
TSS	500	850	680	680	35	37-150	150	Present	0-30	30	Present
TDS	1000*	1150*	1220*	1220*	7			Present			
COD			160	160		20-91	300	Present	1930*	1800*	Present
pH	12.0-12.9*	11.4-12.4*	8.0	8.0	8.3-9.2*	6.8-8.2	6.9-8.3	Variable	6-9	>9*	6-9
Oil & Grease			1.2	1.2		1.6	5.5				
Alkalinity	700	1000									
Nitrogen	2.5		16.0	16.0		0.5	5.0				
Phosphorus	0.05		0.25-1.0	0.25-1.0		0.5	1.5				
Phenol									12		
Temperature, °C (maximum)	40	50			12-31	13					

Note:
B - Batch Operation
C - Continuous Operation
K - Thousand
M - Million
* See Appendix 5 for parameters which may be inhibitory to biological systems.

In some asbestos-cement pipe plants (A), water used in the hydrotest operation may be completely recirculated. Consideration should be given to piping wastewaters from wet saws to the save-all systems. In the asbestos-cement sheet subcategory (B), complete recirculation is possible most of the time. The manufacturing process may be so balanced that the fresh water intake equals the amount of water in the wet product. Fresh water enters the system only for boiler make-up and as part of the vacuum pump seal water. In the asbestos-paper subcategories (C, D), partial recycle of water and underflow solids is attainable. Complete recycle on a continuous basis is possible in asbestos millboard (E) if some provision is made for the release of save-all overflow when upsets occur or product changes are anticipated. In the roofing and floor tiles subcategories (F,G), the possibility of eliminating the contact cooling water operations should be considered. Bearing leaks should be controlled and escaping water protected from contact with wax, oils, glue, and dirt. In any case, non-contact cooling water and condensate should not be mixed with cooling water. In asbestos textile coating (H), the recommended control measure is the containment of wastes in undiluted form and containerization for salvage or land disposal. Dry cleaning techniques should be substituted for wet methods. In addition, measures should be taken to eliminate or contain spills and dripped materials. Since recovery of the solvent is not a goal in vapor absorption (J), an incinerator could be utilized to remove the vapor from the exhaust air. The use of an incinerator would eliminate the wastewater discharge in this subcategory. In wet dust collection (K), if wastewater treatment beyond sedimentation is indicated, the possibility of substituting dry dust collectors for the wet scrubbers should be investigated, thereby eliminating the discharge of wastewater in this subcategory.

Treatment Technology

The process wastewaters from the manufacture of asbestos-cement pipe (A), asbestos-cement sheet (B), and millboard (E) represent the major source of pollutant constituents in the asbestos manufacturing industry. The wastes originate from several points in the manufacturing processes but are usually combined into a single discharge from the plant. The various wastewater treatment practices for each of the subcategories are summarized in Table 8-23-2.

TABLE 8-23-2

ASBESTOS MANUFACTURING INDUSTRY WASTEWATER TREATMENT PRACTICES

REMOVAL EFFICIENCIES (Percent)

POLLUTANT AND METHOD	Asbestos-Cement Pipe A	Asbestos-Cement Sheet B	Asbestos Paper (SB) C	Asbestos Paper (EB) D	Asbestos Millboard E	Asbestos Roofing F	Asbestos Floor Tile G	Coating or Finishing of Textiles H	Solvent Recovery I	Vapor Absorption J	Wet Dust Collection K
BOD											
1. Sedimentation and Coagulation			77	77							
2. Dilution and Lagoon									98		
COD											
1. Sedimentation and Filtration						78					
2. Sedimentation and Coagulation							75				
3. Carbon Adsorption									97	97	
Suspended Solids											
1. Sedimentation and Gravity Thickening	94	96									
2. Sedimentation and Coagulation			96	96			80				98
3. Sedimentation and Filtration						90					
pH*											
1. Neutralization	9	9									

*Effluent level

1. General Industry Description

The rubber processing industry includes the manufacture of tires and inner tubes, synthetic and reclaimed rubber, molded, extruded, fabricated and latex-based products. Each of the above segments of the industry requires varying services and raw materials.

The rubber processing industry has the following Standard Industrial Classification (SIC) numbers: 2822, 3011, 3021, 3031, 3041, 3069, 3293, 7534.

2. Industrial Categorization

The rubber processing industry is broadly subdivided into three main categories: tire and inner tube industry, synthetic rubber industry, and fabricated and reclaimed rubber industry. The waste volumes, waste loads and significant pollutants vary with the operation being conducted and the raw materials used. For the purposes of raw waste characterization and delineation of pretreatment information, the industry is further subdivided into 11 subcategories, as shown in Table 8-24-1. The code letters shown after the subcategories are used to identify them throughout this section. The general molded, extruded, and fabricated rubber products segment has been subcategorized by facility size, as determined by usage of raw materials.

3. Process Description

Tire and Inner Tube (A)

Today's tire manufacturer produces many types of tires designed for a multitude of uses. General product categories include passenger, truck and bus, farm tractor and implement, and aircraft. Basically, the tire consists of five parts, namely: the tread, the sidewall, the cord, the bead, and the inner liner. Basic tire ingredients are synthetic rubbers, natural rubber, fillers, extenders and reinforcers, curing and accelerator agents, antioxidants, and pigments. The typical tire manufacturing process consists of the following:

1. Preparation or compounding of the raw materials;
2. Transformation of compounded materials into the five tire components;
3. Building, molding, and curing of the final product.

TABLE 8-24-1

RUBBER PROCESSING

Main Category	Subcategory	
1. Tire and Inner Tube	Tire and Inner Tube	(A)
2. Synthetic Rubber	Emulsion crumb rubber	(B)
	Solution crumb rubber	(C)
	Latex rubber	(D)
3. Fabricated and Reclaimed Rubber	Small-sized general molded, extruded and fabricated rubber plants	(E)
	Medium-sized general molded, extruded and fabricated rubber plants	(F)
	Large-sized general molded, extruded and fabricated rubber plants	(G)
	Wet digestion reclaimed rubber	(H)
	Pan, dry digestion, and mechanical reclaimed rubber	(I)
	Latex-dipped, latex-extruded and latex-molded rubber	(J)
	Latex foam	(K)

The flow diagram for a typical tire plant is shown in Figure 8-24-1. The Banbury mixer and the roller mill are the basic machinery units used in the compounding operation. Fillers, extenders, reinforcing agents, pigments, and antioxidants are added and mixed into the raw rubber stock. Non-reactive rubber stock, which contains no curing agents, has a long shelf life and may be stored for later use. The reactive rubber stock, which contains curing agents, has a short shelf life and must be compounded and used immediately.

Carbon black and oil are added to the rubber in the compounding operation. After mixing, the compound is sheeted out in a roller mill, extruded into sheets or pelletized. The sheeted material is tacky and must be coated with a soapstone solution to prevent sticking.

The sheeted rubber and other raw materials, such as cord and fabric, are then transformed into one of the basic tire components by several parallel processes. The tire is built up as a cylinder on a collapsible, rotating drum. The uncured tires are sprayed with release agents before molding and curing in an automatic press. After the molding and curing operation, the tire proceeds to the grinding operation where the excess rubber which escaped through the weepholes is ground off. For whitewall tires, additional grinding is required to remove a black protective strip, followed by a protective coat of paint. After inspection and possibly final repairs, the tire is ready to be shipped.

Inner tube manufacture is very similar to tire manufacture and consists of the same three basic steps: compounding of raw materials, extension of compounded materials, and the building, molding and curing operations to form the final product. One distinction of inner tube manufacture is the high usage of butyl rubbers. A flow diagram of a typical inner tube plant is shown in Figure 8-24-2.

Wastewater contaminants from the tire and inner tube industry are: oils from run off, roller mills, hydraulic system, and presses; organics and solids from Banbury seals, soaptone dip tank, dipping operation, spray painting operation, and air pollution equipment discharges; and solvent based cements from the cementing operation.

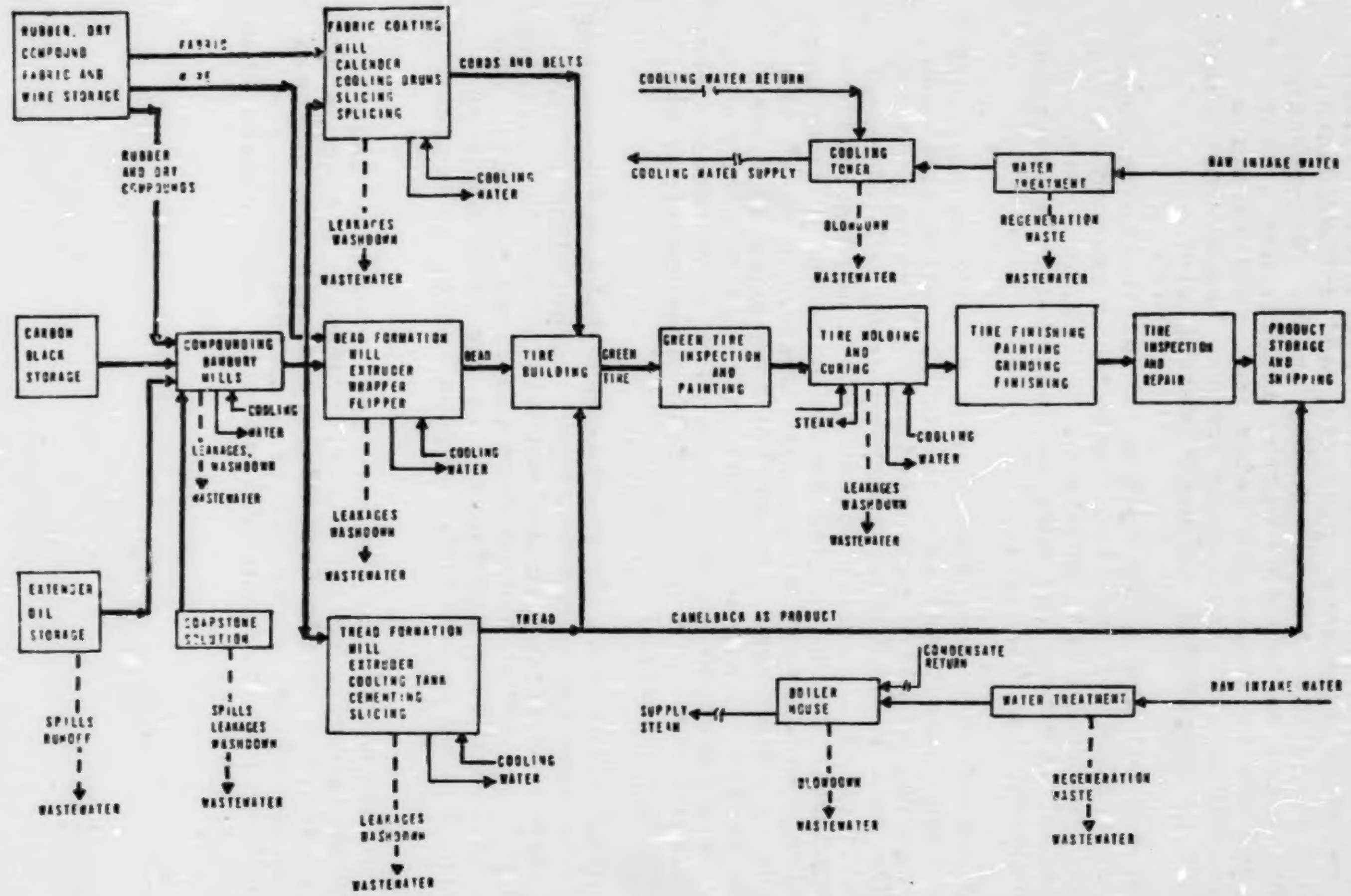

RUBBER, DRY COMPOUND FABRIC AND WIRE STORAGE
FABRIC
WIRE
RUBBER AND DRY COMPOUNDS
CARBON BLACK STORAGE
EXTENDER OIL STORAGE
SPILLS RUNOFF
WASTEWATER
COMPOUNDING BANBURY MILLS
COOLING WATER
LEAKAGES, & WASHDOWN
WASTEWATER
SOAPSTONE SOLUTION
SPILLS LEAKAGES WASHDOWN
WASTEWATER
FABRIC COATING MILL CALENDER COOLING DRUMS SLICING SPLICING
COOLING WATER
LEAKAGES WASHDOWN
WASTEWATER
CORDS AND BELTS
BEAD FORMATION MILL EXTRUDER WRAPPER FLIPPER
BEAD
COOLING WATER
LEAKAGES WASHDOWN
WASTEWATER
TREAD FORMATION MILL EXTRUDER COOLING TANK CEMENTING SLICING
COOLING WATER
LEAKAGES WASHDOWN
WASTEWATER
TREAD
TIRE BUILDING
GREEN TIRE
GREEN TIRE INSPECTION AND PAINTING
TIRE MOLDING AND CURING
STEAM
COOLING WATER
LEAKAGES WASHDOWN
WASTEWATER
TIRE FINISHING PAINTING GRINDING FINISHING
TIRE INSPECTION AND REPAIR
PRODUCT STORAGE AND SHIPPING
CAMELBACK AS PRODUCT
COOLING WATER RETURN
COOLING WATER SUPPLY
COOLING TOWER
BLOWDOWN
WASTEWATER
WATER TREATMENT
REGENERATION WASTE
WASTEWATER
RAW INTAKE WATER
CONDENSATE RETURN
SUPPLY STEAM
BOILER HOUSE
BLOWDOWN
WASTEWATER
WATER TREATMENT
REGENERATION WASTE
WASTEWATER
RAW INTAKE WATER

FIGURE 8-24-1
TIRE AND CAMELBACK PRODUCTION FACILITY (A)
RUBBER INDUSTRY

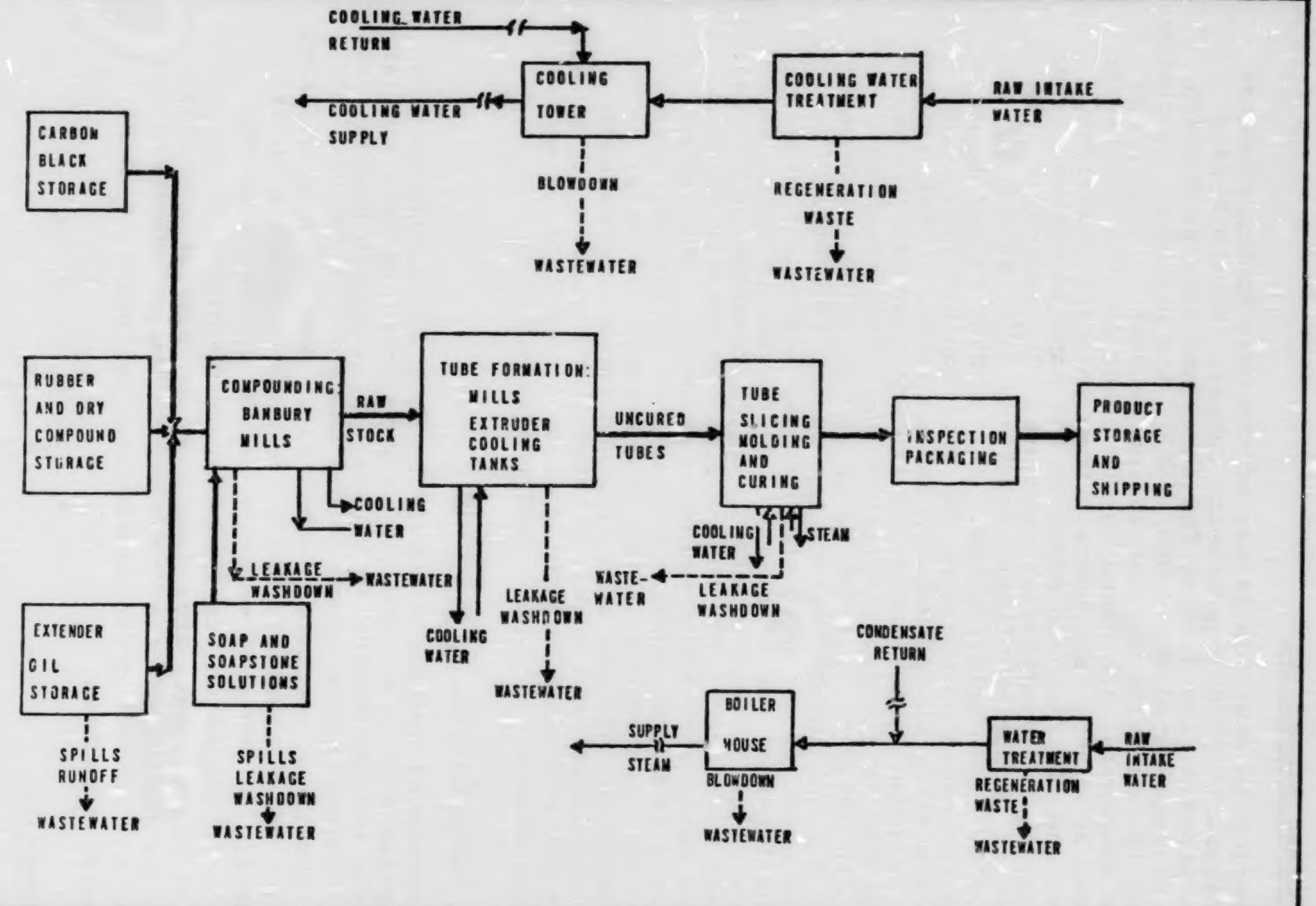

COOLING WATER RETURN
COOLING TOWER
COOLING WATER SUPPLY
COOLING WATER TREATMENT
RAW INTAKE WATER
BLOWDOWN
WASTEWATER
REGENERATION WASTE
WASTEWATER
CARBON BLACK STORAGE
RUBBER AND DRY COMPOUND STORAGE
EXTENDER OIL STORAGE
SPILLS RUNOFF
WASTEWATER
COMPOUNDING: BANBURY MILLS
RAW STOCK
COOLING WATER
LEAKAGE WASHDOWN
WASTEWATER
SOAP AND SOAPSTONE SOLUTIONS
SPILLS LEAKAGE WASHDOWN
WASTEWATER
TUBE FORMATION: MILLS EXTRUDER COOLING TANKS
COOLING WATER
LEAKAGE WASHDOWN
WASTEWATER
UNCURED TUBES
TUBE SLICING MOLDING AND CURING
COOLING WATER
STEAM
LEAKAGE WASHDOWN
WASTE-WATER
INSPECTION PACKAGING
PRODUCT STORAGE AND SHIPPING
CONDENSATE RETURN
BOILER HOUSE
SUPPLY STEAM
BLOWDOWN
WASTEWATER
WATER TREATMENT
RAW INTAKE WATER
REGENERATION WASTE
WASTEWATER

FIGURE 8-24-2
INNER TUBE (A)
RUBBER INDUSTRY

Emulsion Crumb Rubber (B)

Polymerization in emulsion is one of the most common processing techniques to produce synthetic rubber. Figure 8-24-3 shows the process flow diagram for the continuous production of crumb styrene-butadiene rubber (SBR), the principal synthetic rubber, by the emulsion polymerization process. Styrene and butadiene (monomers) are piped to the plant and the inhibitors are removed by caustic scrubbers. Soap solution, catalyst, activator, and modifier are added to the monomer mixture prior to entering the polymerization reactors. The reactor system is capable of producing either "cold" (40-45°F, 0-15 psig) or "hot" (122°F, 40-6- psig) rubber. The product rubber is formed in the emulsion phase of the reaction mixture. The product is a milky white emulsion called latex. Short stop solution is added to the latex leaving the reactors to stop polymerization at the desired conversion. The unreacted monomers are stripped from the latex and recycled to the feed area. An antioxidant to protect the rubber from attack by oxygen and ozone is added to the stripped latex in a blend tank. The latex is now stabilized, and different batches, recipes or dilutions can be mixed. After coagulation, screening, rinsing and dewatering, the rubber crumb is finally dried, pressed in bales and stored prior to shipment. Wastewater contaminants from the emulsion polymerization process are: dissolved and separable organics from monomer recovery, crumb dewatering, monomer stripping and tanks and reactors; uncoagulated latex from tanks, reactors, and monomer stripping; and suspended and dissolved solids from coagulation, crumb dewatering, monomer stripping, and reactors.

Solution Crumb Rubber (C)

The production of synthetic rubber by solution polymerization is a stepwise operation, and, in many aspects, is very similar to emulsion polymerization (B). However, solution polymerization requires extremely pure monomers and the solvent (hexane, for example) should be completely anhydrous. Moreover, in contrast to emulsion polymerization, where the monomer conversion is approximately 60 percent, solution polymerization achieves conversion levels which are typically in excess of 90 percent. Wastewater contaminants are: dissolved and separable organics from solvent purification and monomer recovery; suspended and dissolved solids from crumb dewatering; and high alkalinity from caustic scrubbers.

Latex Rubber (D)

Latex production follows the same processing steps as emulsion crumb production with the exception of latex coagulation, crumb rinsing, drying and baling. The polymerization is carried out to 98 to 99 percent conversion levels. As a result, monomer

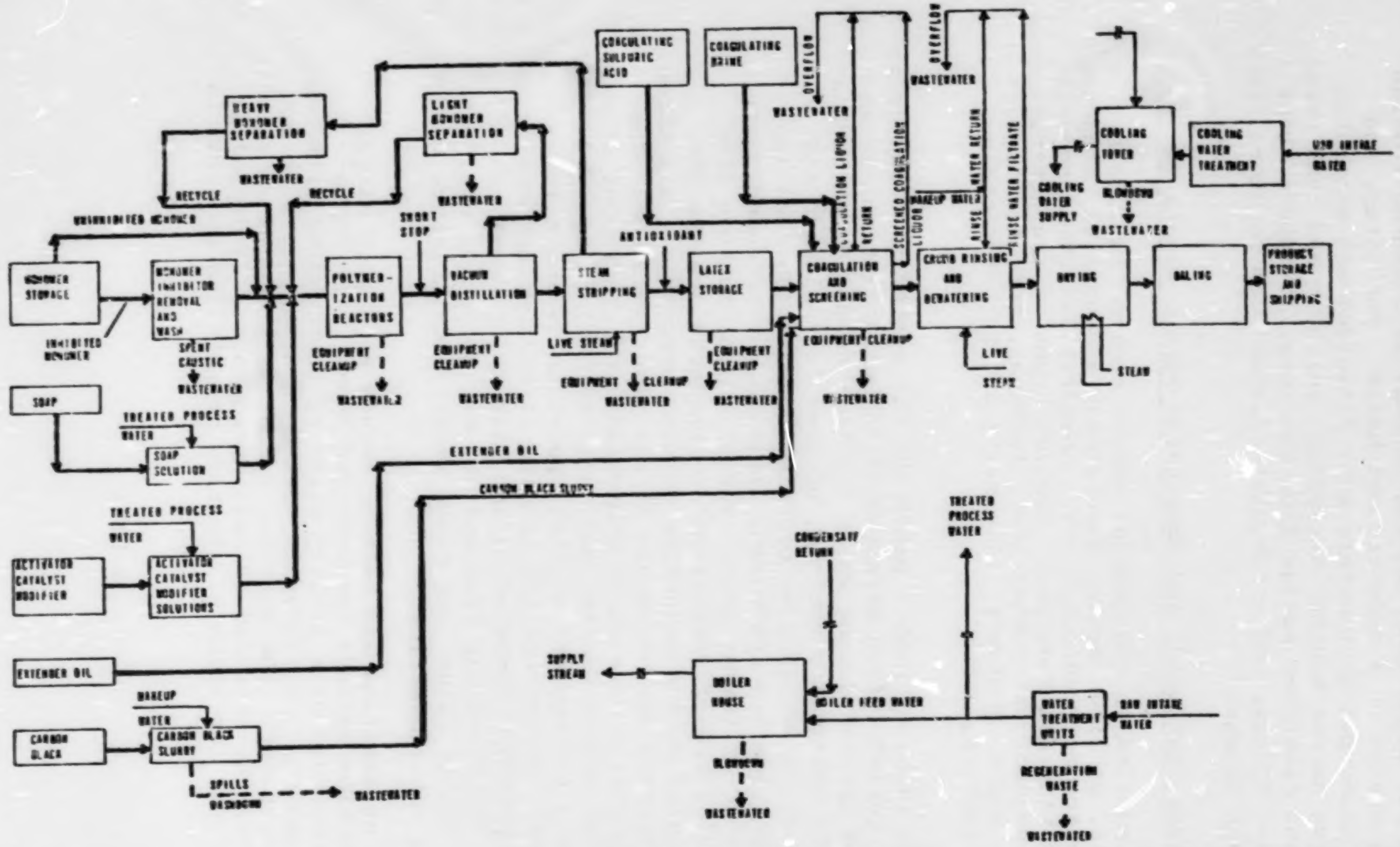

MONOMER STORAGE
INHIBITED MONOMER
MONOMER INHIBITOR REMOVAL AND WASH
SPENT CAUSTIC
WASTEWATER
UNINHIBITED MONOMER
SOAP
TREATED PROCESS WATER
SOAP SOLUTION
ACTIVATOR CATALYST MODIFIER
ACTIVATOR CATALYST MODIFIER SOLUTIONS
EXTENDER OIL
CARBON BLACK
MAKEUP WATER
CARBON BLACK SLURRY
SPILLS WASHDOWN
HEAVY MONOMER SEPARATION
LIGHT MONOMER SEPARATION
RECYCLE
POLYMERIZATION REACTORS
EQUIPMENT CLEANUP
SHORT STOP
VACUUM DISTILLATION
STEAM STRIPPING
LIVE STEAM
ANTIOXIDANT
LATEX STORAGE
COAGULATING SULFURIC ACID
COAGULATING BRINE
OVERFLOW
COAGULATION LIQUOR
RETURN
SCREENED COAGULATION LIQUOR
COAGULATION AND SCREENING
MAKEUP WATER
RINSE WATER RETURN
RINSE WATER FILTRATE
CRUMB RINSING AND DEWATERING
LIVE STEAM
DRYING
STEAM
BALING
PRODUCT STORAGE AND SHIPPING
COOLING TOWER
COOLING WATER SUPPLY
BLOWDOWN
COOLING WATER TREATMENT
RAW INTAKE WATER
EXTENDER OIL
CARBON BLACK SLURRY
CONDENSATE RETURN
TREATED PROCESS WATER
SUPPLY STEAM
BOILER HOUSE
BOILER FEED WATER
WATER TREATMENT UNITS
REGENERATION WASTE

FIGURE 8-24-3
EMULSION CRUMB RUBBER PRODUCTION FACILITY (B)
RUBBER INDUSTRY

recovery is not economical and the process is directed towards maximum conversion on a once-through basis. The nature and origins of principal wastewaters are: dissolved and separable organics from excess monomer stripping, reactors and tank cars; suspended and dissolved solids from reactors, strippers, tank cars and tank trucks; and uncoagulated latex from reactors, tank cars and tank trucks.

General Molded, Extruded, and Fabricated Rubber Plants (E, F, G)

Product categories in the general molded segment include battery parts, seals, packing, heels, shoes, medical supplies, druggist supplies, stationery supplies, etc. General extruded products includes belting and sheeting. Product types in the general fabricated segment are rubber hose, footwear, friction tape, fuel tanks, boats, pontoons, life rafts and rubber clothing and coated fabrics, etc.

During the molding of rubber products, the rubber is cured as it is shaped. Curing (often referred to as vulcanization) is an irreversible process during which a rubber compound, through a change in its chemical structure, becomes less plastic and more resistent to swelling by organic liquids. In addition, elastic properties are conferred, improved, or extended over a greater range of temperature. The principal methods used for the manufacture of general molded products are the compression, transfer, and injection molding processes. All three of these processes may be in use at one plant location. The processes typically consist of compounding of the rubber stock, preparation of mold preforms, molding, and deflashing. A process flow diagram for a typical molding operation is shown in Figure 8-24-4. The nature and origins of wastewaters are: oils from curing presses, compounding and pick-up by storm run-off; solids from soapstone dip tank and wet air pollution equipment discharges; rubber fines from rinse water; and anti-tack agents from cooling water overflow.

Manufacture of sheeting and belting serves as a good example of the production methods for extruded items. The rubber stock is compounded on a Banbury mixer or compounding mill. After compounding, the rubber is worked on a warm-up mill and fed to the extruder. The extruded rubber is produced as sheets. In some cases, the extruded or calendared rubber is dipped in soapstone slurry for storage. Belting or extruded sheeting is

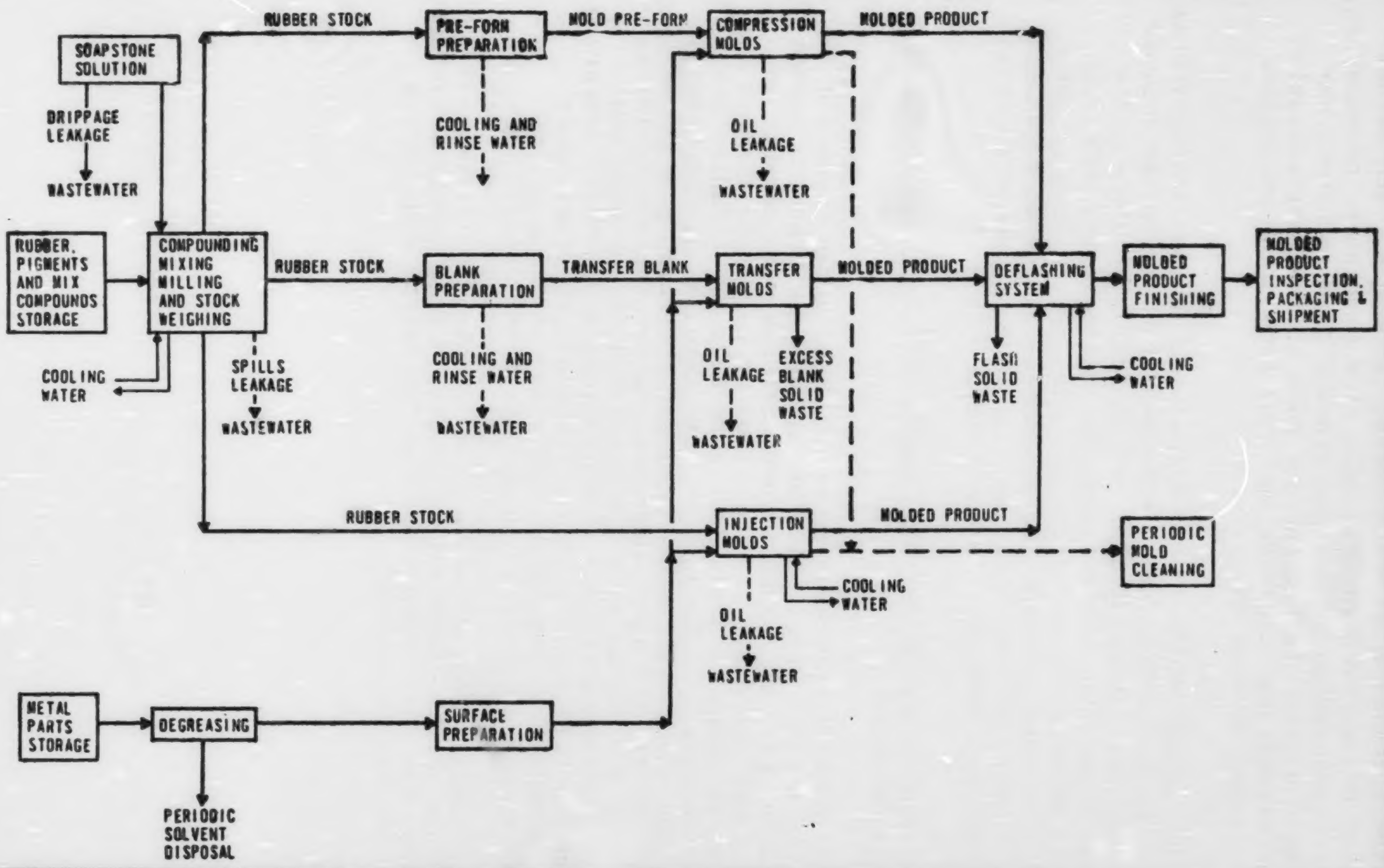

SOAPSTONE SOLUTION
DRIPPAGE LEAKAGE
WASTEWATER
RUBBER, PIGMENTS AND MIX COMPOUNDS STORAGE
COMPOUNDING MIXING MILLING AND STOCK WEIGHING
COOLING WATER
SPILLS LEAKAGE
WASTEWATER
RUBBER STOCK
PRE-FORM PREPARATION
COOLING AND RINSE WATER
MOLD PRE-FORM
COMPRESSION MOLDS
OIL LEAKAGE
WASTEWATER
MOLDED PRODUCT
RUBBER STOCK
BLANK PREPARATION
COOLING AND RINSE WATER
WASTEWATER
TRANSFER BLANK
TRANSFER MOLDS
OIL LEAKAGE
WASTEWATER
EXCESS BLANK SOLID WASTE
MOLDED PRODUCT
DEFLASHING SYSTEM
FLASH SOLID WASTE
COOLING WATER
MOLDED PRODUCT FINISHING
MOLDED PRODUCT INSPECTION, PACKAGING & SHIPMENT
RUBBER STOCK
INJECTION MOLDS
MOLDED PRODUCT
COOLING WATER
OIL LEAKAGE
WASTEWATER
PERIODIC MOLD CLEANING
METAL PARTS STORAGE
DEGREASING
PERIODIC SOLVENT DISPOSAL
SURFACE PREPARATION

Figure 8-24-4

FLOW DIAGRAM FOR THE PRODUCTION OF A TYPICAL MOLDED ITEM (E,F,G) cured using a rotacure or press curing technique. The nature and origins of wastewaters are: oils from machinery, calendering, extrusion, compounding, and storm run-off from storage area; solids from the anti tack agent and tank and wet air pollution equipment discharges; organics and lead from steam vulcanizer condensate; and cooling water.

Hose production provides a good example of the fabricated rubber manufacturing processes. Figure 8-24-5 illustrates the process flow diagram for the manufacture of typical hose items. The nature and origins of wastewaters contaminants are: oils from machinery,compounding, and storm run-off; solids from soapstone dip tank, ply formation and latex storage; dissolved organics from ply formation, shoe building, and latex storage; and anti-tack agents from cooling water overflow.

Wet Digestion Reclaimed Rubber (H) and Pan, Dry Digestion and Mechanical Reclaimed Rubber (I)

Reclaimed rubber is prepared primarily from scrap tires and scrab inner tubes. Three basic techniques are used to produce reclaimed rubber: the digester process, the pan process, and the mechanical process. A generalized process flow diagram for the three processes is shown in Figure 8-24-6. Broadly, the reclaiming process can be divided into three major components, two of which are mostly mechanical and the third predominantly chemical. By far the most important source of raw material is tire scrap. The rubber scrap is separated and ground, then given heat treatment for depolymerization, and finally processed for intensive friction milling. All three processes employ similar rubber-scrap separation and size-reduction methods. They differ in depolymerization and the final processing steps. The nature and origins of wastewater contaminants are: oil from depolymerization, blowdown tank, dewatering, dryers and compounding; solids, caustics and organics from depolymerization, defibering, dewatering and soapstone dip tanks; and fibrous material removed from tires.

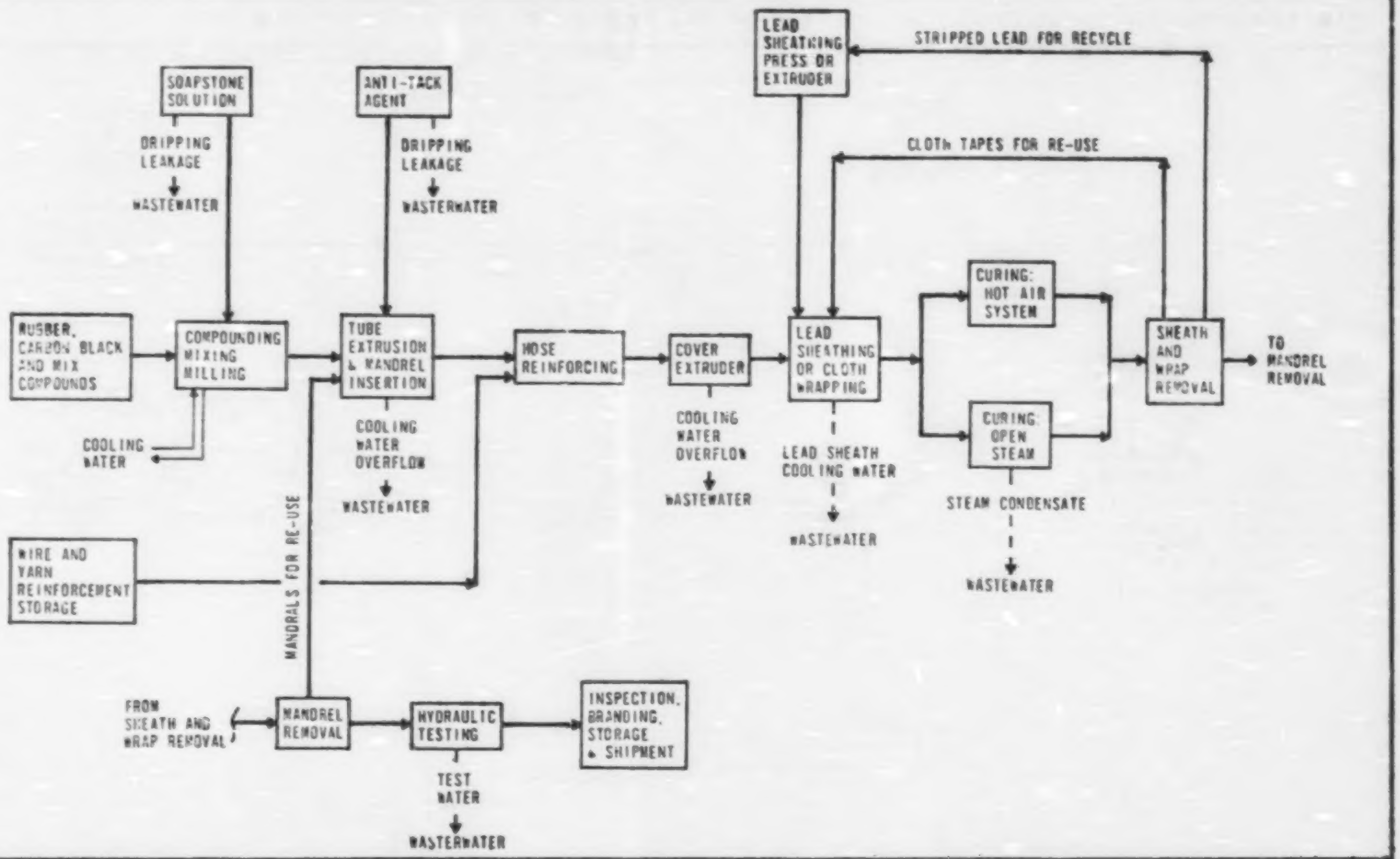
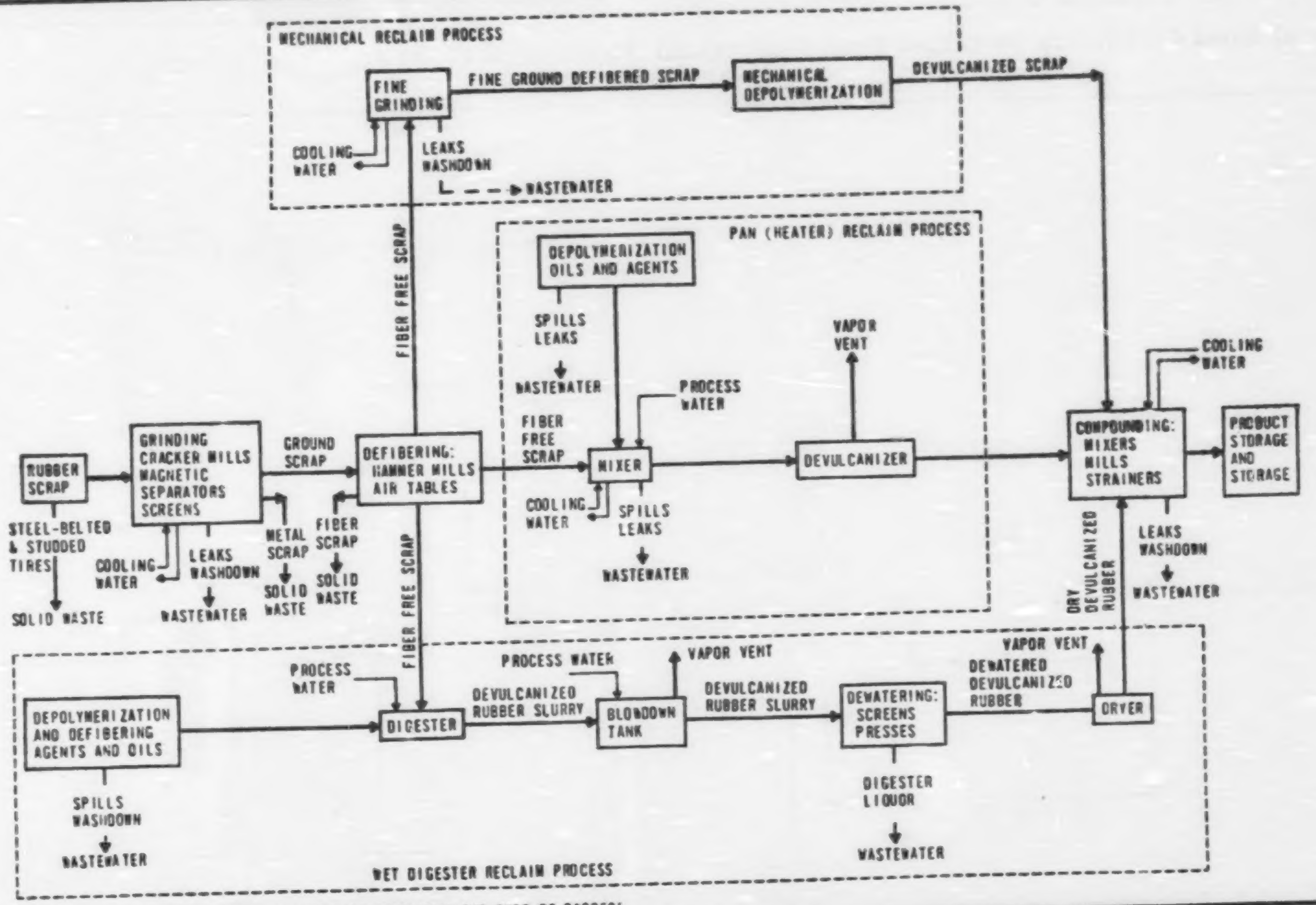

RUBBER, CARBON BLACK AND MIX COMPOUNDS
SOAPSTONE SOLUTION
DRIPPING LEAKAGE
WASTEWATER
COMPOUNDING MIXING MILLING
COOLING WATER
ANTI-TACK AGENT
DRIPPING LEAKAGE
WASTERWATER
TUBE EXTRUSION & MANDREL INSERTION
COOLING WATER OVERFLOW
WASTEWATER
MANDRALS FOR RE-USE
WIRE AND YARN REINFORCEMENT STORAGE
HOSE REINFORCING
COVER EXTRUDER
COOLING WATER OVERFLOW
WASTEWATER
LEAD SHEATHING PRESS OR EXTRUDER
LEAD SHEATHING OR CLOTH WRAPPING
LEAD SHEATH COOLING WATER
WASTEWATER
CURING: HOT AIR SYSTEM
CURING: OPEN STEAM
STEAM CONDENSATE
WASTEWATER
SHEATH AND WRAP REMOVAL
TO MANDREL REMOVAL
STRIPPED LEAD FOR RECYCLE
CLOTH TAPES FOR RE-USE
FROM SHEATH AND WRAP REMOVAL
MANDREL REMOVAL
HYDRAULIC TESTING
TEST WATER
WASTERWATER
INSPECTION, BRANDING, STORAGE & SHIPMENT

FIGURE 8-24-5

FLOW DIAGRAM FOR THE PRODUCTION OF TYPICAL HOSE ITEMS (INCLUDING REINFORCED TYPES) (E,F,G)


MECHANICAL RECLAIM PROCESS
FINE GRINDING
FINE GROUND DEFIBERED SCRAP
MECHANICAL DEPOLYMERIZATION
DEVULCANIZED SCRAP
COOLING WATER
LEAKS WASHDOWN
WASTEWATER
FIBER FREE SCRAP
PAN (HEATER) RECLAIM PROCESS
DEPOLYMERIZATION OILS AND AGENTS
SPILLS LEAKS
WASTEWATER
PROCESS WATER
FIBER FREE SCRAP
MIXER
COOLING WATER
SPILLS LEAKS
WASTEWATER
VAPOR VENT
DEVULCANIZER
RUBBER SCRAP
STEEL-BELTED & STUDDED TIRES
SOLID WASTE
GRINDING CRACKER MILLS MAGNETIC SEPARATORS SCREENS
COOLING WATER
LEAKS WASHDOWN
WASTEWATER
METAL SCRAP
SOLID WASTE
GROUND SCRAP
DEFIBERING: HAMMER MILLS AIR TABLES
FIBER SCRAP
SOLID WASTE
COMPOUNDING: MIXERS MILLS STRAINERS
COOLING WATER
PRODUCT STORAGE AND STORAGE
LEAKS WASHDOWN
WASTEWATER
DRY DEVULCANIZED RUBBER
FIBER FREE SCRAP
DEPOLYMERIZATION AND DEFIBERING AGENTS AND OILS
SPILLS WASHDOWN
WASTEWATER
PROCESS WATER
DIGESTER
DEVULCANIZED RUBBER SLURRY
PROCESS WATER
VAPOR VENT
BLOWDOWN TANK
DEVULCANIZED RUBBER SLURRY
DEWATERING: SCREENS PRESSES
DIGESTER LIQUOR
WASTEWATER
DEWATERED DEVULCANIZED RUBBER
VAPOR VENT
DRYER
WET DIGESTER RECLAIM PROCESS

NOTE: SOME RECLAIMING FACILITIES OPERATE MORE THAN ONE TYPE OF PROCESS

FLOW DIAGRAM OF TYPICAL MECHANICAL, PAN (HEATER), AND WET DIGESTER RECLAIM PROCESSES (H,I)

Figure 8-24-6

Latex-Dipped, Latex-Extruded and Latex-Molded Rubber (J) and Latex Foam (K)

To manufacture sundry rubber goods from latex compounds, it is necessary to convert the compounds into solids of desired form. The latex is compounded with various ingredients, such as antioxidants. Several manufacturing processes are used for fabricating different types of rubber goods from latex mixtures. The process diagrams for a typical latex-based dipped item and a latex foam item are shown in Figures 8-24-7 and 8-24-8 respectively. Principal wastewater contaminants for the latex-dipped, latex-extruded, and latex-molded rubber are suspended solids, dissolved solids, oil and surfactants. An important additional contaminant for the latex foam is zinc.

4. Wastewater Characterization

Wastewater characteristics of total effluents from each of the 11 subcategories of the rubber processing industry are shown in Table 8-24-2.

5. Control and Treatment Technology

In-plant Control

Significant in-plant control of both waste quantity and quality is possible for most subcategories of the rubber processing industry. For tires and inner tubes (A), in-plant control includes the proper handling of soapstone, latex dip, and discharges from air pollution control equipment. A closed-loop recirculation system eliminates the continuous discharge of large quantities of soapstone. Alternatives to recirculation include the discharge of soapstone directly to the process sewers or the use of substitute solutions which require the system to be cleaned on a less frequent basis. A common practice among the larger manufacturers is to eliminate the latex dipping operation from the tire facility. In plants that still dip fabric, an effective control measure is to seal off drains, supply the area with curbing, and drum the waste solutions for landfill disposal. The solids from the wet scrubber discharge in the tire-finishing area can be settled out in a sump. The particulates are large, and with a properly designed separator, the clarified water can be completely reused. Further in-plant measures for the tire and inner tube industry include the control of spills and leakage by providing curbing and oil sumps, the use of dry sweeping equipment for

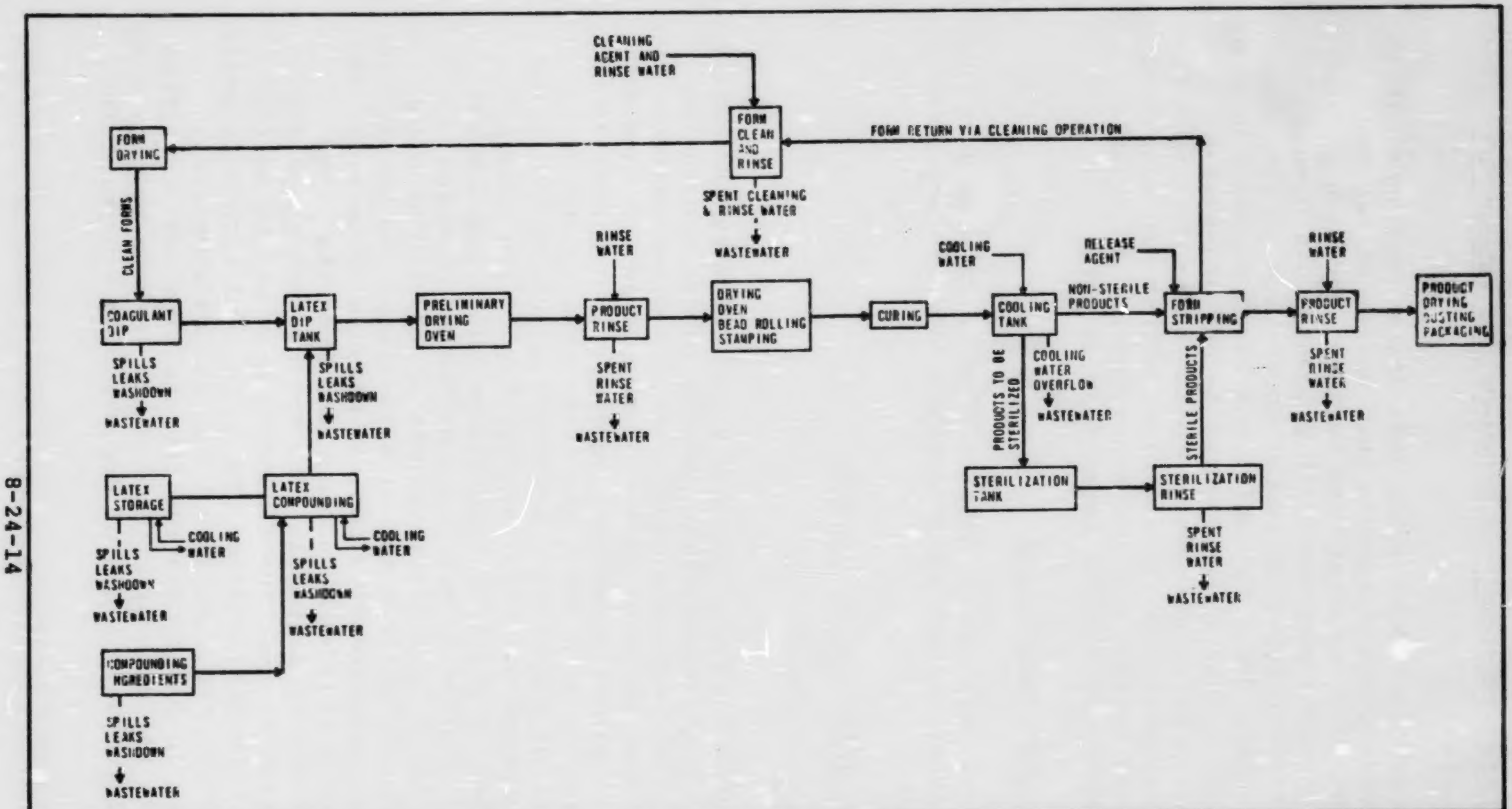

CLEANING AGENT AND RINSE WATER
FORM CLEAN AND RINSE
FORM RETURN VIA CLEANING OPERATION
FORM DRYING
SPENT CLEANING & RINSE WATER
WASTEWATER
CLEAN FORMS
RINSE WATER
COOLING WATER
RELEASE AGENT
RINSE WATER
NON-STERILE PRODUCTS
COAGULANT DIP
LATEX DIP TANK
PRELIMINARY DRYING OVEN
PRODUCT RINSE
DRYING OVEN BEAD ROLLING STAMPING
CURING
COOLING TANK
FORM STRIPPING
PRODUCT RINSE
PRODUCT DRYING DUSTING PACKAGING
SPILLS LEAKS WASHDOWN
WASTEWATER
SPILLS LEAKS WASHDOWN
WASTEWATER
SPENT RINSE WATER
WASTEWATER
PRODUCTS TO BE STERILIZED
COOLING WATER OVERFLOW
WASTEWATER
STERILE PRODUCTS
SPENT RINSE WATER
WASTEWATER
LATEX STORAGE
LATEX COMPOUNDING
STERILIZATION TANK
STERILIZATION RINSE
COOLING WATER
SPILLS LEAKS WASHDOWN
WASTEWATER
COOLING WATER
SPILLS LEAKS WASHDOWN
WASTEWATER
SPENT RINSE WATER
WASTEWATER
COMPOUNDING INGREDIENTS
SPILLS LEAKS WASHDOWN
WASTEWATER

Figure 8-24-7
FLOW DIAGRAM FOR THE PRODUCTION OF TYPICAL LATEX-BASED DIPPED ITEMS (J)

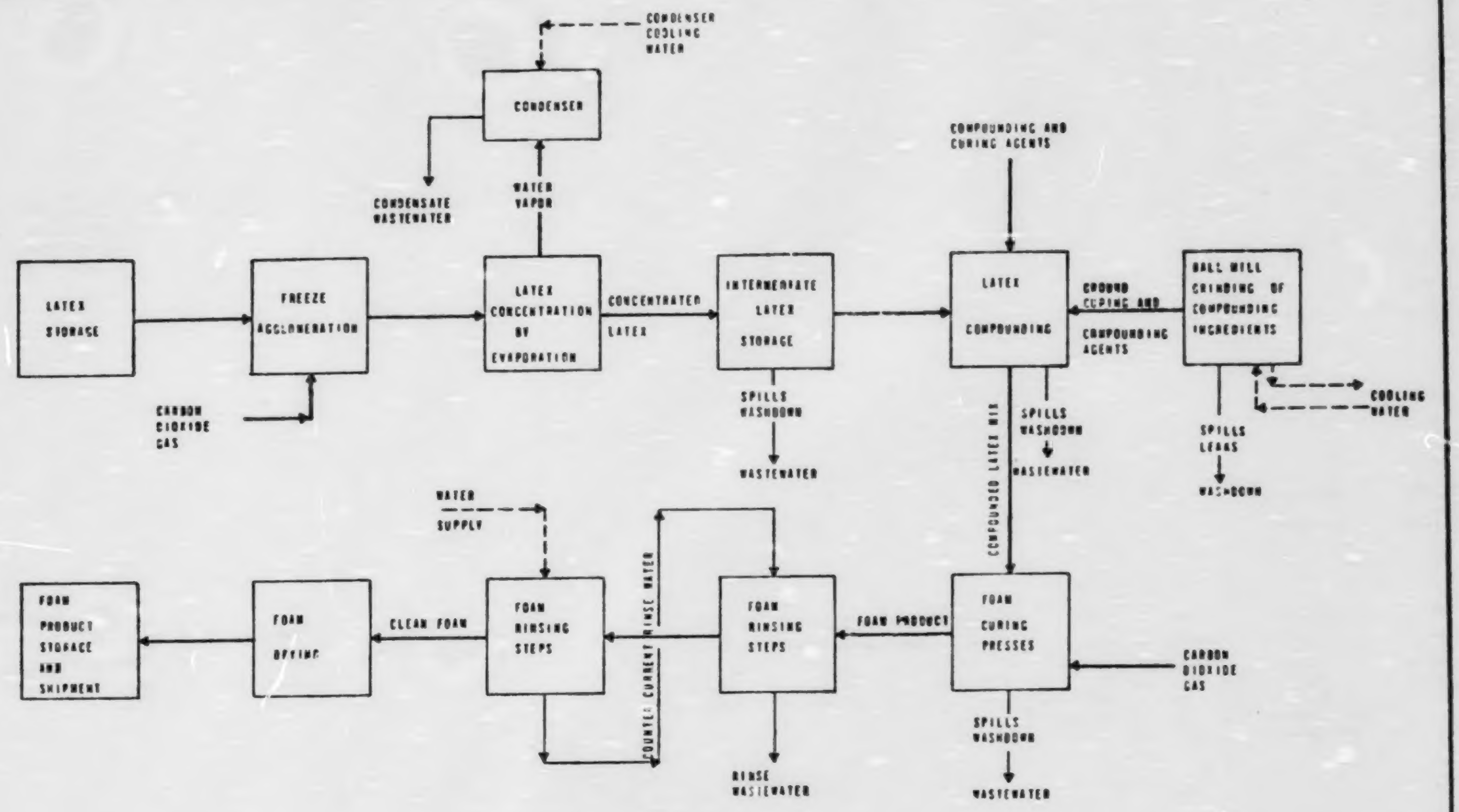

CONDENSER COOLING WATER
CONDENSER
CONDENSATE WASTEWATER
WATER VAPOR
COMPOUNDING AND CURING AGENTS
LATEX STORAGE
FREEZE AGGLOMERATION
LATEX CONCENTRATION BY EVAPORATION
CONCENTRATED LATEX
INTERMEDIATE LATEX STORAGE
LATEX COMPOUNDING
GROUND CURING AND COMPOUNDING AGENTS
BALL MILL GRINDING OF COMPOUNDING INGREDIENTS
COOLING WATER
CARBON DIOXIDE GAS
SPILLS WASHDOWN
WASTEWATER
SPILLS WASHDOWN
WASTEWATER
COMPOUNDED LATEX MIX
SPILLS LEAKS
WASHDOWN
WATER SUPPLY
FOAM PRODUCT STORAGE AND SHIPMENT
FOAM DRYING
CLEAN FOAM
FOAM RINSING STEPS
COUNTER CURRENT RINSE WATER
FOAM RINSING STEPS
FOAM PRODUCT
FOAM CURING PRESSES
CARBON DIOXIDE GAS
RINSE WASTEWATER
SPILLS WASHDOWN
WASTEWATER

FIGURE 8-24-8
LATEX FOAM (K)
RUBBER INDUSTRY

TABLE 8-24-2
RUBBER PROCESSING INDUSTRY
RAW WASTEWATER CHARACTERIZATION

Parameter (mg/l)	Tire & Inner Tube A	Emulsion Crumb B	Solution Crumb C	Latex Rubber D	Small-Sized Rubber Plants E	Medium-Sized Rubber Plants F	Large-Sized Rubber Plants G	Wet Digestion & Mechanical Reclaimed Rubber H	Pan, Dry Digestion & Mechanical Reclaimed Rubber I	Latex-dipped, Latex-extruded & Latex-Molded Rubber J	Latex Foam K
Flow Range (gallons per day)	0.2MM-22.22MM	1.42MM-4.34MM	.21MM-2.75MM	.18MM-.226MM	1.5M-6.27M	24M-285.4M	.14MM-1.92MM	1.32MM	.89MM	24.5M-49M	.42MM
Flow Type		C	C								
BOD$_5$ (mg/l)	0.2-31	115-183	10-123	377-418	4-24	10-24	6-28	10	7.2	133-152	1155*
TSS	9-1065	124-770	18-451	450-470	1-9	1-13	10-62	21	16.6	78-3019	492
TDS	0-757				384-657	607-790	213-3,100*	132	104	385-1146*	1353*
COD	0-298	528-1886*	50-1168*	2440*-2790*	3-20	20-50	57-261	52	37.6	176-678	4285*
Oil	1-96*	7-191*	8-195*	28	1-26	.8-7	4.6-31	4.7	2.8	6-129*	571*
Lead						.008	0-8.0*				
Surfactants										1.8-6.4	5.1
Zinc											200*

Note: M - thousand
MM - million
C - continuous process
* See Appendix 5 for parameters which may be inhibitory to biological systems.
Data shown is from exemplary plants, and may not be typical of all plants in the industry.

prevention of process-area washdowns from contaminating wastewaters, and the diking of all oil-storage areas to prevent contamination of wastewaters by oil spillages.

Since the synthetic rubber industry (B, C, D) is highly technological and involves numerous proprietary and confidential processing techniques, many of the significant control methods would call for radical changes in the processing or product quality and are, therefore, not feasible. However, some potential exists in the control of crumb rinse overflow, coagulation liquor overflow, vacuum systems seal water, carbon black slurries, latex spills and baler oil leaks. Reduction of COD levels in the synthetic rubber wastewaters through the use of activated carbon technology is also feasible.

In-plant control measures for the general molded, extruded, and fabricated rubber subcategories (E, F, G) require proper handling and isolating general spills and leaks of soapstone and other anti-tack agents, latex compounds, solvents and rubber cements, metal preparation wastes, and air pollution control equipment discharges. Contamination by machinery oils, greases and suspended solids can be reduced by blocking of floor drains, removing oil leaks promptly with dry absorbent granules and by curbing the problem area. The spillage of soapstone and other anti-tack solutions can be controlled by similar methods. An effective way to handle latex is the use in latex drums of plastic liners which can be discarded when the drum is reused. Latex spills around storage and transfer facilities are coagulated with alum and scraped from the ground. Solvents and rubber cements should be mixed and stored in areas without floor drains to control spills and leaks. If acid pickling is used to prepare metal components, precipitation of metals and pH adjustment should be carried out. The pickling wastes can also be containerized and hauled from the plant.

In the wet digestion reclaimed rubber subcategory (H), significant in-plant control measures include the defibering of scrap rubber by mechanical or physical techniques as an alternative to chemical defibering and the return of process oils and digestor liquor. Return of process oils and the control of vapor condensates and spills and leaks are significant in-plant measures for the pan, dry digestion and mechanical reclaimed rubber subcategory (I). In the latex-based products subcategories (J, K), prevention of latex spills and leaks,and reduction in the volumes of foam rinse waters and cleaning wastes by employing countercurrent rinsing, constitute the most significant in-plant control measures.

Treatment Technology

The various wastewater treatment practices for each of the 11 subcategories of the rubber processing industry are summarized in Table 8-24-3. The removal efficiencies shown pertain to the raw waste loads of process effluents from each of the subcategories.

TABLE 8-24-3
RUBBER PROCESSING INDUSTRY
WASTEWATER TREATMENT PRACTICES

Removal Efficiency (Per Cent)

Pollutant and Method	Tire & Inner Tube A	Emulsion Crumb Rubber B	Solution Crumb Rubber C	Latex Rubber D	Small Converter E	Medium Converter F	Large Converter G	Wet Digestion H	Dry Digestion I	Latex J	Latex Foam K
BOD											
1. Sedimentation and Holding Lagoon Recirculation of Soapstone	76-83		99							70	
2. Coagulation, Clarification		82	81	51							
3. Coagulation, Settling, Activated Sludge			81	86							
4. Coagulation, Clarification, Zinc Precipitation, Clarification											65
COD											
1. Sedimentation and Holding Lagoon Recirculation of Soapstone	62-87		78							32	
2. Coagulation, Clarification		72-74	74	80							
3. Coagulation, Settling, Activated Sludge			52	76							
4. Oil Separator and Holding Lagoon							44-63	94*	9		
Oil and Grease											
1. Sedimentation Recirculation of Soapstone	96		91								
2. Gravity Separator	60						95	99.8*	93	28	
3. Coagulation, Clarification		99	99	52							
4. Coagulation, Settling, Activated Sludge			88								
Suspended Solids											
1. Coagulation, Clarification		89		81						73	
2. Equalization, Activated Sludge			83	62							
3. Settling, Stabilization Lagoon			89-94								
4. Gravity Separator	80						72	99*	82		
5. Coagulation, Clarification, Zinc Precipitation and Clarification											90

Note: *Values indicated reflect reductions due to recycle as well as wastewater treatment.

1. General Industry Description

The Timber products processing industry includes a broad spectrum of operations ranging from cutting and removing the timber from the forest, to the processing of the timber into a wide variety of finished products.

Establishments engaged in this industry are included in Standard Industrial Classifications (SIC) 24 and 25.

2. Industrial Categorization

This industry has been divided into the following subcategories:

Subcategory	Designation
Barking	A
Veneer	B
Plywood	C
Hardboard-Dry Process	D
Hardboard-Wet Process	E
Wood Preserving	F
Wood Preserving-Steam	G
Wood Preserving-Boultonizing	H
Wet Storage	I
Log Washing	J
Sawmills and Planing	K
Finishing	L
Particleboard	M
Insulation Board (subject to change)	N
Insulation Board with Steam or Hardboard Production	O
Wood Furniture and Fixture Production without Spray Booths or Laundry Facilities	Q
Wood Furniture and Fixture Production without Spray Booths but with Laundry	R
Wood Furniture and Fixture Production with Spray Booths, without Laundry	
Wood Furniture and Fixture Production with Spray Booths, with Laundry	

Process Descriptions

Figure 8-25-1 contains a product manufacturing flow diagram for the timber industry, which includes the subcategories discussed below.

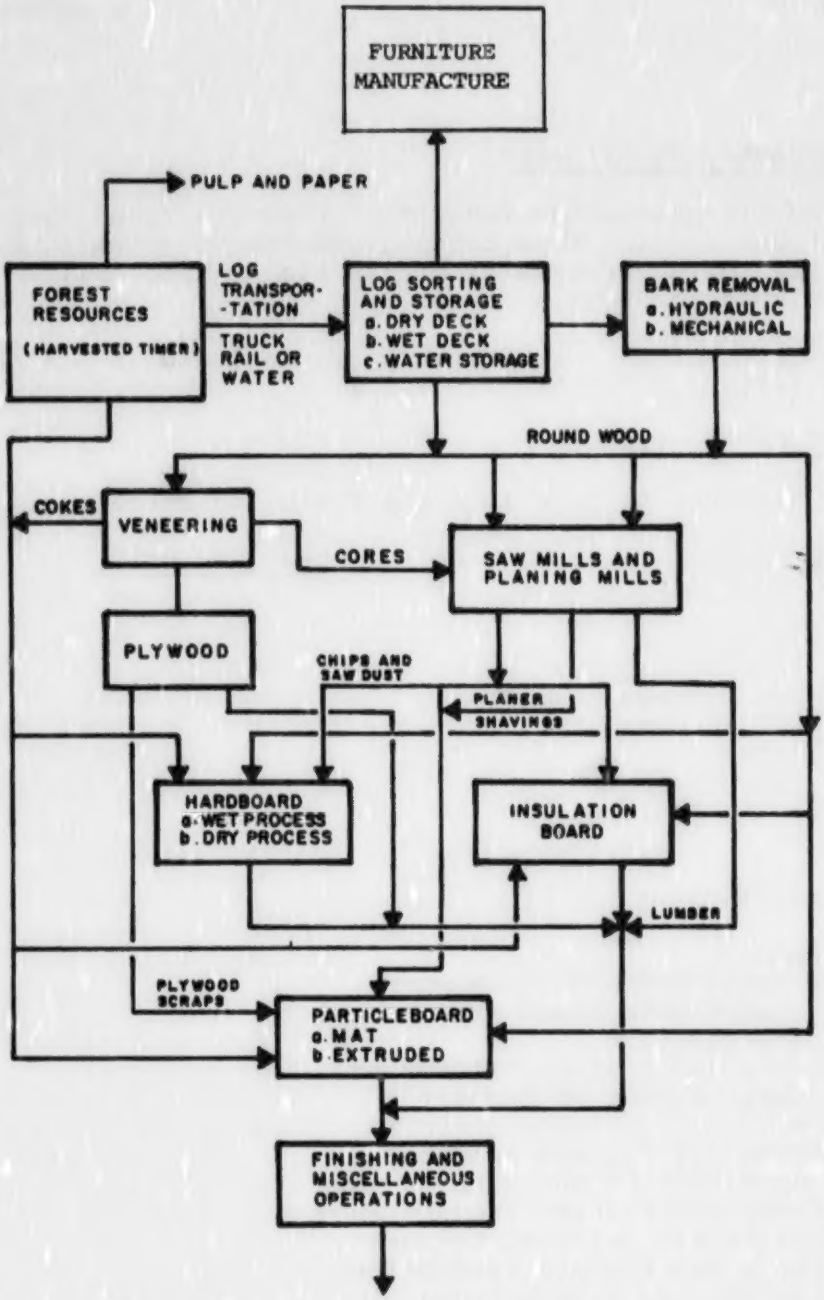

FURNITURE MANUFACTURE
PULP AND PAPER
FOREST RESOURCES (HARVESTED TIMER)
LOG TRANSPOR-TATION
TRUCK RAIL OR WATER
LOG SORTING AND STORAGE a. DRY DECK b. WET DECK c. WATER STORAGE
BARK REMOVAL a. HYDRAULIC b. MECHANICAL
ROUND WOOD
COKES
VENEERING
CORES
SAW MILLS AND PLANING MILLS
PLYWOOD
CHIPS AND SAW DUST
PLANER SHAVINGS
HARDBOARD a. WET PROCESS b. DRY PROCESS
INSULATION BOARD
LUMBER
PLYWOOD SCRAPS
PARTICLEBOARD a. MAT b. EXTRUDED
FINISHING AND MISCELLANEOUS OPERATIONS

FIGURE 8-25-1
INTERRELATIONSHIPS OF THE TIMBER PRODUCTS INDUSTRY

Barking (A) - The barking subcategory includes operations which involve the removal of bark from logs. Barking may be accomplished by several types of mechanical abrasion or by hydraulic force. Types of barking machines include: drum barkers, ring barkers, bag barkers, hydraulic barkers and cutterhead barkers. The hydraulic barker uses a high pressure water jet to blast bark from the log. Large volumes of water are required for this operation, and large volumes of wastewater are produced. Due to the high quality water requirement of the operation, water recycle is not usually practiced at the present time.

The remaining barkers remove bark by milling, scraping and abrasion. The ring and cutterhead barkers use no water. Drum and bag barkers employ the use of water sprays to reduce dust, promote thawing of wood in cold climates, or to reduce the bond between bark and wood. Wastewaters high in BOD are generated from the wet barking processes. The BOD level present in barking wastewaters is dependent on the type or species of tree being barked and the degree of recycling being practiced.

Veneer and Plywood (B,C) - Plywood is an assembly of layers of wood (veneer) joined together by means of an adhesive. Hardwood plywood is generally used for decorative purposes and has the "face ply" of wood from deciduous or broad leaf trees. Softwood plywood is generally used for construction and structural purposes, and the veneers are of wood from coniferous or needle bearing trees. The principal unit process in the manufacturing of veneers is the cutting of the veneer. The particular cutting method used determines the appearance of a plywood panel.

Prior to cutting the veneer, the logs may be conditioned by steam treatment or by immersion in a hot water vat. Wastewaters are high in BOD, COD and total solids.

Freshly cut veneers must be dried in order to avoid attack by molds and fungi and to render them compatible with the gluing process. Surfaces of veneer dryers accumulate wood particles and pitch, which may be removed by scraping followed by flushing with water or by blowing with air. Generally pitch must be dissolved by detergent washing and rinsing. The nature and quantity of this wastewater varies according to the amount of water used, the amount of scraping prior to application of water, condition and operation of the dryer, and the species of wood being dried. Most driers are equipped with deluge systems to extinguish fires that start inside the drier. Fire deluge water can add significantly to the wastewater problems in some cases.

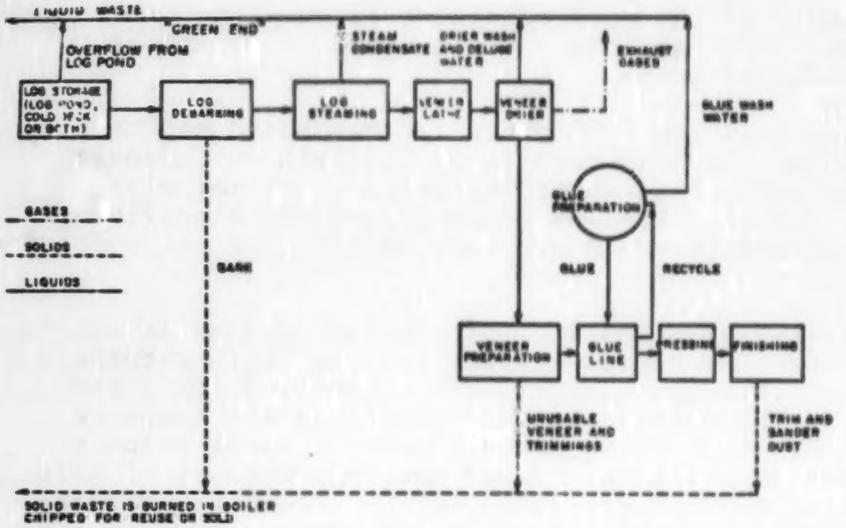
A number of adhesives can be used in the gluing operations. The glue is mixed and then applied by means of a spreader. The glue system must be cleaned regularly to avoid build-up of dried glue. Wastewaters are high in BOD, COD and total solids.

After gluing, the layers of veneer are subjected to pressure to insure proper alignment and intimate contact between the wood layers and the glue. After the pressing operation any number of finishing operations can take place. These include redrying, trimming, sanding, sorting, molding, and storing. Figure 8-25-2 contains a process flow diagram for veneer and plywood production.

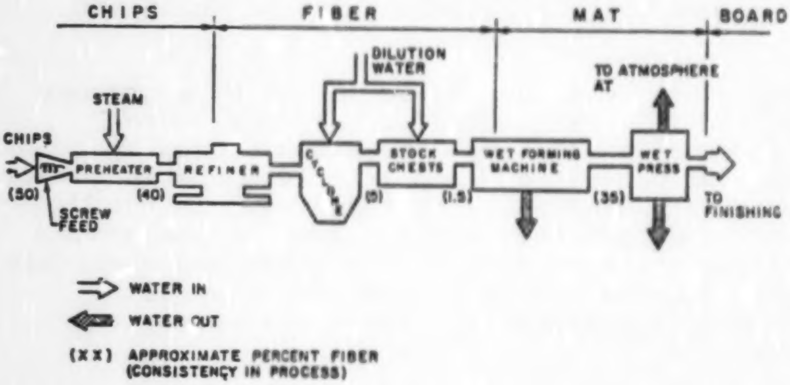
Hardboard (D,E) - Hardboard is manufactured by reducing wood materials to the fibrous state and putting them back together in the form of sheets or boards. In the wet process (E) water is used as the medium for carrying the fibers and distributing them in the forming machine; part of the carrying water is removed and a slight amount of pressing is done. The mats are then transferred to a press for additional pressing. In the dry process (D) air serves as the carrying and distributing medium. Figure 8-25-2 contains a flow diagram for hardboard manufacturing. Logs or wood scraps must be either processed to chips at the hardboard manufacturing plant or off-site. The wood chips are then pretreated or softened with steam prior to pulping. The two major pulping processes are the explosion process and the thermal plus mechanical refining. In the explosion process wood chips are subjected to high temperature steam in a "gun", or high pressure vessel, and ejected through a quick opening valve. Upon ejection the softened chips burst into a mass of wood fibers. The second process, which consists of softening the fibers with heat and then mechanically pulping the wood chips is more widely used. The mechanical pulping takes place in disc refiners or attrition mills. After the addition of additives to the pulp, the pulp is ready for delivery to the board former to begin the process of reassembling the fibers into hardboard.

In the wet process the mat is usually formed on a fourdrinier type machine similar to those used in paper making. The wood pulp is diluted and is then passed onto an endless traveling wire screen. The water is removed by gravity through the screen, and then further moisture is removed by suction. Additional water is removed as the sheet passes through rollers. The water removed in the mat formation is recycled. However, periodic purging constitutes a waste stream.

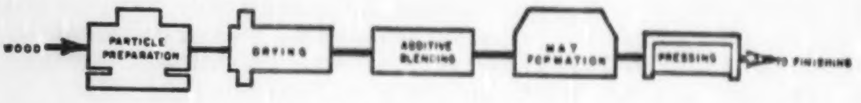
In the dry process the fibers are suspended in air rather than water. The prepared fibers are fed by a volumetric feeder to the "felting unit" where the fibers are distributed onto a moving screen at the floor of the felter. Air is sucked through the screen to aid in the felting. Periodic cleaning of the press plates constitutes a waste stream.


LIQUID WASTE
GREEN END
OVERFLOW FROM LOG POND
STEAM CONDENSATE
DRIER WASH AND DELUGE WATER
EXHAUST GASES
LOG STORAGE (LOG POND, COLD DECK OR BOTH)
LOG DEBARKING
LOG STEAMING
VENEER LATHE
VENEER DRIER
GLUE WASH WATER
GLUE PREPARATION
GASES
SOLIDS
LIQUIDS
BARK
GLUE
RECYCLE
VENEER PREPARATION
GLUE LINE
PRESSING
FINISHING
UNUSABLE VENEER AND TRIMMINGS
TRIM AND SANDER DUST
SOLID WASTE IS BURNED IN BOILER
CHIPPED FOR REUSE OR SOLD

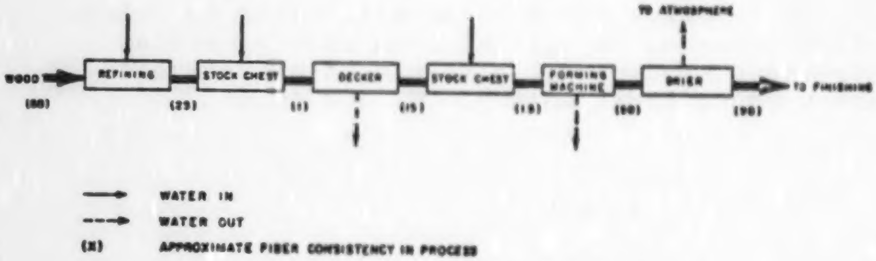
Veneer and Plywood
(B, C)


CHIPS
FIBER
MAT
BOARD
DILUTION WATER
TO ATMOSPHERE AT
STEAM
CHIPS
PREHEATER
REFINER
CYCLONE
STOCK CHESTS
WET FORMING MACHINE
WET PRESS
(50)
(40)
(5)
(1.5)
(35)
SCREW FEED
TO FINISHING
WATER IN
WATER OUT
(XX) APPROXIMATE PERCENT FIBER (CONSISTENCY IN PROCESS)

Wet Process
Hardboard Mill
(E)


WOOD
PARTICLE PREPARATION
DRYING
ADDITIVE BLENDING
MAT FORMATION
PRESSING
TO FINISHING

Particleboard (H)


TO ATMOSPHERE
WOOD
REFINING
STOCK CHEST
DECKER
STOCK CHEST
FORMING MACHINE
DRIER
TO FINISHING
(88)
(23)
(1)
(15)
(15)
(90)
(90)
WATER IN
WATER OUT
(X) APPROXIMATE FIBER CONSISTENCY IN PROCESS

Insulationboard (G)

FIGURE 8-25-2
TIMBER PRODUCTS

When the reassembly of the wood particles is completed the fibers are welded together into a tough, durable grainless board on the hardboard press.

After being discharged from the press the hardboard may be oil tempered by bathing the hardboard in an oil bath to increase its hardness, strength, and water resistance. It may also receive a paint finish. The wet process produces significant quantities of wastewater which are high in BOD, COD and suspended solids.

Wood Preserving (F,G,H) - The wood preserving process is one in which round and sawn wood products are injected with chemicals that provide fungistic and insecticidal properties, or impart fire resistance. The most common preservatives are creosote, pentachlorophenol, and various formulations of water soluble inorganic chemicals. Fire retardents are formulations of salts including borates, phosphates, and ammonium compounds. Treatment is accomplished by either pressure or non-pressure processes. The pressure process employs a combination of air, hydrostatic pressure and vacuum procedures. Non-pressure processes utilize open tanks and either hot or cold preservatives in which the wood is immersed.

Some woods are conditioned by either steam (G) or by a process called Boultonizing (H) in order to render the stock more penetrable to preservative treatment. Steaming is usually carried out at 245°F for periods of from 1 to 16 hours in the same vessel in which the preservative is injected. In the Boultonizing process wood is heated under vacuum in the vessel at 180° - 220°F. Wastewaters contain preservative and chemicals used in the process; leachate from the wood including oils, phenolic compounds, and carbohydrates. These discharges exert a high oxygen demand.

Wet Storage (I) - The harvesting of timber is seasonal in most parts of the United States. Consequently, log storage is often essential for continuous mill production. In addition, preservation of the raw material while in storage is necessary to insure that the quality of the product is not impaired. Storage and preservation techniques usually involve the use of water. When logs are stored on land, they must be sprayed with water to prevent the ends from cracking. Logs may also be stored in log ponds, river impoundments, or directly in marine or estuarine waters. Wood products consisting of planer shavings, sawdust, and bark are stored in piles and sprayed with water to reduce dust. Runoff from spraying as well as from rain generates leachate. Wastewaters produced as a result of storage and preservation are high in total solids, COD and color.

Log Washing (J) - Logs are sometimes washed by applying water from fixed nozzles for the purpose of removing foreign material from the surface of the log before further processing. This process results in improved fuel quality (if used as a fuel) or increased saw life. When logs are stored in a body of water the benefits of log washing are accomplished. Wash waters contain settleable solids and can be recycled.

Sawmills and Planing Mills (K) - This subcategory includes the timber products processing operations of sawing, resawing, edging, trimming, planing, and/or machining.

The term "headrig" is used by the industry to include all the machinery which is utilized to produce the initial breakdown of a log into boards. Subsequent sawing operations reduce the thickness of the lumber and square the edges. The lumber may be passed through a preservative and sold or it may be air or kiln dried. Water usage at sawmill operations vary significantly. A majority of sawmills use no process water at all. On the other hand, a sawmill producing power, washing logs, and practicing wet storage of logs may use over 10 million gallons of water per day. Wastewater characteristics from the latter are discussed elsewhere.

Finishing (L) - Finishing operations include drying, dipping, staining, coating, moisture proofing, machining, fabricating and by-product utilization. Machining is the process of shaping wood to a desired form (shakes, shingles, flooring) and generates no wastewaters. Fabrication involves the production of crates, windows, mobile dwellings and is accomplished by mechanical fastening or adhesives. The use of adhesives normally necessitates a certain amount of wastewater because of cleanup operations. By-product utilization involves the production of pressed logs, chair seats, etc. and are insignificant sources of wastewater. The only source of wastewaters result from the washing of equipment. Because of the wide variety of finished products and their methods of application, wastewaters can be expected to contain a wide variety of constituents.

Particleboard (M) - Particleboard is defined as board products that are composed mainly of distinct particles of wood (not reduced to fibers) which are bonded together with an organic or inorganic binder. Figure 8-25-2 contains a flow diagram for particleboard processing.

Wood residues are mechanically reduced, classified by size and shape, dried, blended with additives, and formed into a uniform mat on a forming machine. After the formation of a mat it is pressed, cut and finished. Finishing operations include sanding, planing and coating. Fires are a frequent occurance in this operation.

Wastewaters are generated from equipment washups, cooling and mat sprays, air pollution control equipment, and fire suppression water. Contaminants include resins (urea or phenols), oils, wax, wood fibers, finishing materials (stains, dyes, coatings), depending upon the particular materials utilized in the operation.

Insulation Board (N,O) - Insulation board is a fiberboard produced from wood in a fibrous state. Those plants that precondition the raw material with steam are included in subcategory O, while those that do not subject the wood material to steam pressure are included in subcategory N.

Seventy percent of the raw material for this industry is in the form of wood chips, which are washed in order to remove grit, dirt, sand and metal. Wash water is usually recycled. Wood then enters the refining machine where it is fiberized and diluted in preparation for mat formation. Drying and finishing operations are similar to particleboard (L) operations. Large quantities of wastewater are present containing leachable materials from the wood and additives added during the process. Discharges are characterized by high quantities of BOD, COD, suspended solids, and dissolved solids. Figure 8-25-2 contains a flow diagram for Insulationboard processing.

Wood Furniture and Fixture Production(P,Q,R,S) - The principal raw materials used in furniture manufacturing are lumber, veneer, plywood, hardboard and particleboard. The materials are cut, planed, sanded, bent by steam application, and assembled with glue and/or metal fasteners. The furniture is then finished in a variety of operations including bleaching, staining, filling, sealing and topcoating.

The various finishing materials may be applied by brush or roller, but most often they are sprayed onto the wood surfaces. Spraying operations require the use of spray booths to collect and contain the overspray and thus provide fire and health protection. The air drawn through the booth is filtered by either a dry or a water wash method. The dry method consists of filtering the air through a filter consisting of paper or fiberglass. In the water wash method, water is brought into contact with the exiting air and removes the impurities. This water stream is the source of wastewaters.

In the larger plants laundry facilities for rag cleaning are common and represent a major wastewater source.

4. Wastewater Characterization

Cleaning operations are the major source of wastewater in this industry, generating intermittent flows. Table 8-25-1 contains raw wastewater characteristics for the various subcategories. Some other pollutant parameters that may be present in process waters of various segments of the timber products processing industry are: pentachlorophenol, dioxins, dinitrophenol, acenapthene, 2;4 - dichlorophenol, benzene, chromium, toluene, ammonia, fluoride, copper, zinc and arsenic.

5. Control and Treatment Technology

In-Plant Control - Wastewater reduction measures in this industry consist primarily of clarifying and recycling techniques. Dry cleaning operations can reduce wastewater flows. In the veneer and plywood industries, the dryers can be scraped prior to washing, thus reducing discharges.

Treatment Technology - Since most timber products are biodegradable, biological treatment is practicable. Table 8-25-2 contains removal efficiencies for different treatment schemes practiced by this industry.

TABLE 8-25-1

RAW WASTE CHARACTERIZATION - TIMBER PRODUCTS INDUSTRY

Waste Parameter	SUBCATEGORIES								
	Log Barking-A	Veneer and Plywood - B,C			Hard Board Dry Process D	Hard Board Wet Process E	Wood Preserving F,G,H	Wet Storage (on land only) I	Log Washing J
		Log Conditioning	Veneer Dryer Washwater	Washing of Glue Tanks and Tanks					
Flow GPD Flow Type		* C	15,000 B	4,000 B	Low Flows	200M-4MM C	20M C	160M-2MM C	384M C
BOD (mg/1)	56-250	300-5,000*	60-900*	400-10,000*		700-4000*	150	3-200	
TSS (mg/1)	500-3000	70-3000	80-5,000	6,000-15,000		220-1700	200-5000	4-125	75-200
COD (mg/1)		1500-15,000*	60-7,000*	9,000-33,000*		2,600-12,000*	2M-30M*	20-200	100-260
PH		3.8*-7				4-5	4-6		
Color	Under 50 Units							30-300	70-300
Phosphates as P(mg/1)		1-6	0-11	6-40		0.3-3		0.5-7	0.1-3
Phenols(mg/1)		0-1	0-5	24-100		0.7-1.0	50-1,000	5-170	80
Oil and Grease (mg/1)							50-600*		

NOTE: M = 1,000
MM = 1,000,000
* See Appendix 5 for parameters which may be inhibitory to biological systems
B - Batch
C - Continuous

TABLE 8-25-1 (Continued)

Waste Parameter	SUBCATEGORIES						
	Sawmills-K Fabrication only	Finishing L	Particleboard M	Insulation Board N,O	FURNITURE MANUFACTURE (1)		
					Spray Booths R	Glue Washwater Q	Laundry Wastes R
Flow GPD Flow Type	530-124M C	20-400 B	50-86M C & B	416M-3MM C & B	1500-5M(per wk) B	5-1600(per wk) B	200-5M(per wk) B
BOD (mg/1)	700-16,000*		6-250	300-3000*	130-16,000*	100-300	8,000*
TSS(mg/1)	700-5000	400-250M	30-300	1500-2000	100-40,000	300-9000	18,000
COD(mg/1)	4,000-17000*	8M-245M	100-300	2000-7500*	3,000-100,000*	11,000-40,000*	35,000*
PH	5-11*		6-12*		7-13*	5-9	12*
Color			15-400		40-500	0-400	500
Phosphates as P(mg/1)	1-20	100-6500	0-1				
Phenols(mg/1)	0-300	100-5000	0-20				
Oil and Grease (mg/1)			1-50				

Note: M = 1,000
MM = 1,000,000
B - Batch
C - Continuous
* See Appendix 5 for parameters which may be inhibitory to biological systems
(1) where spray booths and laundries are both utilized, the wastewater characteristics are a composite of the individual values shown.

TABLE 8-25-2

TIMBER MANUFACTURING INDUSTRY
WASTE WATER TREATMENT PRACTICES

REMOVAL (Percent)

POLLUTANT & METHOD	SUBCATEGORIES																
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	Q	R
BOD																	
Primary Clarification with Biological Treatment	85-95				70-97	80-	90	90						78-94			
Containment with Recycle											100						
TSS																	
Primary Clarification with Biological Treatment					0-10									0-99			
Containment with Recycle											100						
COD																	
Primary Clarification with Biological Treatment						60	80										50
Recycle, Equalization, Sedimentation									20								
Containment with Recycle											100						

1. General Industry Description

Paper is made from raw materials including wood, cotton, linen rags, and straw, which contain adequate amounts of cellulose fiber, the basic component. The cellulose is separated from other constituents of the fiber source and fiberized by the pulping process. Today, wood accounts for over 98 percent of the virgin fiber used in papermaking.

Paper is made by depositing, from a dilute water suspension of pulp, a layer of fiber on a fine screen which permits the water to drain through but which retains the fiber layer. This layer is then removed from the wire, pressed and dried.

Establishments engaged in this industry are covered by Standard Industrial Classifications (SIC) 261, 262, 263, 264 and 265.

Wastewaters from this industry contain suspended solids, BOD, COD color, mercury, zinc and PCB's.

2. Industrial Categorization

The unbleached kraft and semichemical pulp segment of this industry has been divided into the following subcategories:

Subcategory	Designation
Unbleached Kraft	A
Sodium Base Neutral Sulfite Semi-Chemical	B
Ammonia Base Neutral Sulfite Semi-Chemical	C
Unbleached Kraft Neutral Sulfite Semi-Chemical (Cross Recovery)	D
Paperboard from Waste Paper	E

"Neutral Sulfite Semi-Chemical shall be referred to as "NSSC" in this description.

The remaining segment of this industry has been tentatively divided into the following subcategories:

1. Groundwood
2. Sulfite
3. Dissolving sulfite
4. Bleached kraft
5. Soda
6. Deinked
7. Non-integrated fine paper
8. Non-integrated tissue paper
9. Non-integrated coarse paper

3. Process Description

Wood Preparation

Wood is received at the mills in various forms and converted to chips for pulping. If the wood is received with the bark on it, the log is washed and the bark is removed by drum, pocket, or hydraulic barkers. Large quantities of wastewaters containing suspended solids and BOD are generated. Barked logs can be chipped directly producing little or no effluent.

Pulping

There are several methods used for pulping wood. In some, the chips are cooked with chemicals under controlled conditions of temperature, pressure, time and pulping liquor composition. The various processes utilize different chemicals or combinations of them. Wood can also be reduced to a fibrous state by mechanical means or a combination of chemical and mechanical action. The repulping of waste paper is a hydraulic and mechanical process. The various pulping methods will be discussed in detail below.

Paper Making

Paper is manufactured in two relatively discreet operations: the dry end and the wet end. Wood pulp enters the paper machine at the wet end where it is diluted to a consistency of 0.25-0.5%.

The pulp is then deposited on a cylinder or wire and the excess machine white water passes through the machine generating a wastewater. The sheet then passes to the forming and pressing section of the machine where more water is removed. It finally passes to the dry end of the machine where the paper is dried. Figure 8-26-1 is a flow diagram of the paper making process.

Unbleached Kraft (A)

Unbleached kraft is the production of pulp without bleaching by a "full cook" process, utilizing a highly alkaline sodium hydroxide and sodium sulfide cooking liquor. This pulp is used principally to manufacture linerboard, the smooth facing of corrugated boxes, grocery sacks and wrapping paper.

Wood chips are fed to a digester, where the chips are cooked to dissolve the lignin and separate the cellulose fibers. The unbleached kraft is called a full-cook process since the fiberizing is completed in the cooking process alone. The pulp, along with the spent cooking liquor is then sent to drum washers where the pulp and the liquor are separated. The pulp is formed into paper. The "weak black liquor" from the wash process, containing solids, inorganic cooking chemicals and organic wood constituents is concentrated to a "strong black liquor". The "strong black liquor" is burned and the heat is recovered. The molten smelt on the furnace floor is dissolved in water to form "green liquor", which is clarified and causticized with lime. After causticizing, the combined sodium sulfide-sodium hydroxide solution is known as "white liquor", and recycled to the pulping process. This operation generates wastewaters high in COD, BOD and suspended solids.

Another source of wastewater is condensate streams. These streams are low in BOD and TSS, but may contain methanol, ethanol, and acetone. This wastewater is recycled back into the pulp wash-water operation in some plants. Figure 8-26-2 is a flow diagram for this process.

Sodium Base Neutral Sulfite Semi-Chemical (B)

This production of pulp without bleaching utilizes a neutral sulfite cooking liquor having a sodium base. Mechanical fiberizing follows the cooking stage. The principal product made from this pulp is the corrugating medium or inner layer in the corrugated box "sandwich". In this process, the wood chips are cooked in either batch or continuous digesters. NSSC refers to the cooking

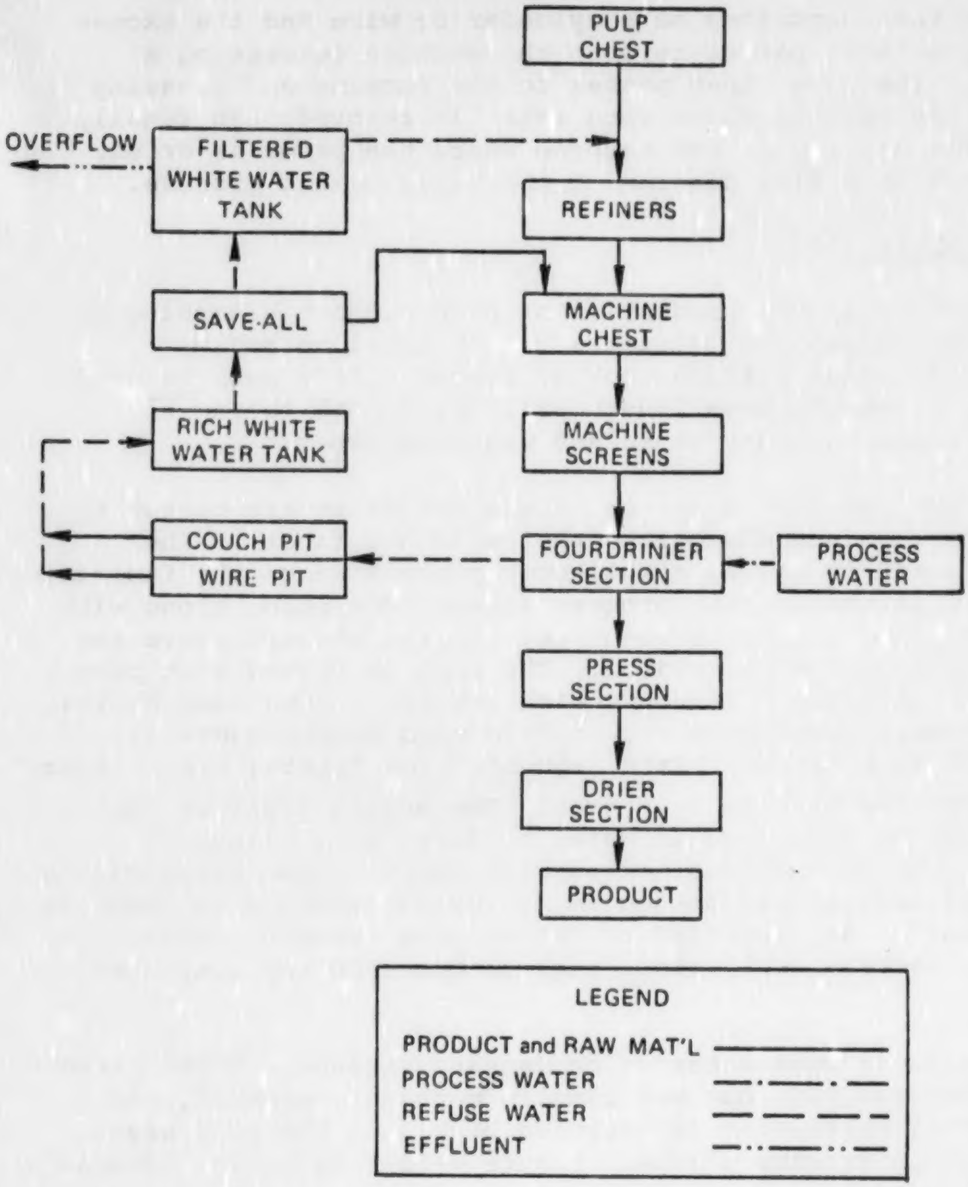

PULP CHEST
OVERFLOW
FILTERED WHITE WATER TANK
REFINERS
SAVE-ALL
MACHINE CHEST
RICH WHITE WATER TANK
MACHINE SCREENS
COUCH PIT
WIRE PIT
FOURDRINIER SECTION
PROCESS WATER
PRESS SECTION
DRIER SECTION
PRODUCT
LEGEND
PRODUCT and RAW MAT'L
PROCESS WATER
REFUSE WATER
EFFLUENT

Figure 8-26-1
Paper Making
Pulp, Paper and Paperboard

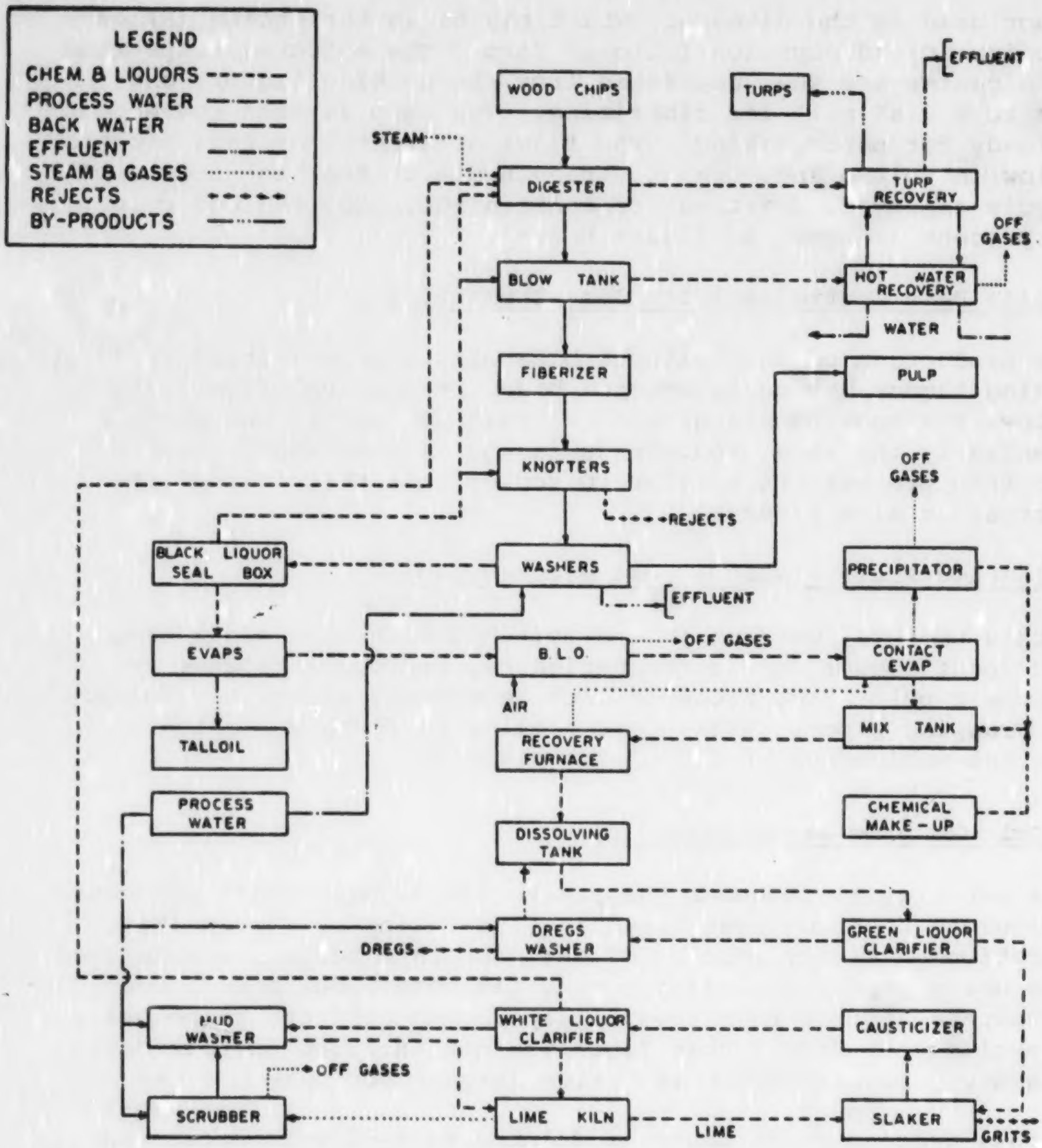

LEGEND
CHEM. & LIQUORS
PROCESS WATER
BACK WATER
EFFLUENT
STEAM & GASES
REJECTS
BY-PRODUCTS
WOOD CHIPS
STEAM
DIGESTER
TURPS
EFFLUENT
TURP RECOVERY
OFF GASES
BLOW TANK
HOT WATER RECOVERY
WATER
FIBERIZER
PULP
KNOTTERS
REJECTS
OFF GASES
BLACK LIQUOR SEAL BOX
WASHERS
EFFLUENT
PRECIPITATOR
EVAPS
B.L.O.
OFF GASES
CONTACT EVAP
AIR
MIX TANK
TALLOIL
RECOVERY FURNACE
PROCESS WATER
CHEMICAL MAKE-UP
DISSOLVING TANK
DREGS WASHER
DREGS
GREEN LIQUOR CLARIFIER
MUD WASHER
WHITE LIQUOR CLARIFIER
CAUSTICIZER
OFF GASES
SCRUBBER
LIME KILN
LIME
SLAKER
GRITS

Figure 8-26-2
Pulp, Paper and Paperboard
Kraft Pulping (A)

liquor used in the digester, which may be in the sodium (B) or ammonium (C) (discussion follows) form. The softened chips from the digester are then separated from the cooking liquor, and sent to a disk mill for fiberizing. The pulp is then washed and is ready for paper making. The final effluent from this process is low in volume and high in strength due to the high degree of recycle employed. Wastewaters contain BOD, COD, TSS and color. The process is shown in Figure 8-26-3.

Ammonia Base Neutral Sulfite Semi-Chemical (C)

This production of pulp without bleaching uses a neutral sulfite cooking liquor having an ammonia base. Mechanical fiberizing follows the cooking stage, and the pulp is used to manufacture essentially the same products as is sodium base NSSC. Wastes from this process are similar to sodium base NSSC, except that nitrogen is also present.

Unbleached Kraft - NSSC (Cross Recovery)(D)

In this process, wood chips are combined with the sodium base NSSC spent liquor (B) in the unbleached kraft (A) process to produce a pulp. The products include grocery sacks, corrugated and wrapping paper. Wastes are similar to those generated from the unbleached kraft pulping plant (A).

Paperboard from Waste Paper (E)

This subcategory includes the production of paperboard products from waste paper without bleaching, de-inking or wood pulping operations. Eighty percent of the fibrous materials are derived from waste papers including corrugated boxes, box board, and newspapers. Mills that produce paperboard products principally or exclusively from virgin fiber are not included in this subcategory. Figure 8-26-4 is a flow diagram for this process.

In this process waste paper is diluted to 4-6% with water, and is then fed to a pulper along with steam. The pulper consists of a vat with rotating impeller blades that shred, rip and finally defiber the waste paper. The pulper can either be batch or continuous in operation. The fibers are separated from the solution, cleaned, and then ready for the paper machines.

The major source of wastewater is in the pulp separation and cleaning operations, and contain components high in BOD, COD and TSS.

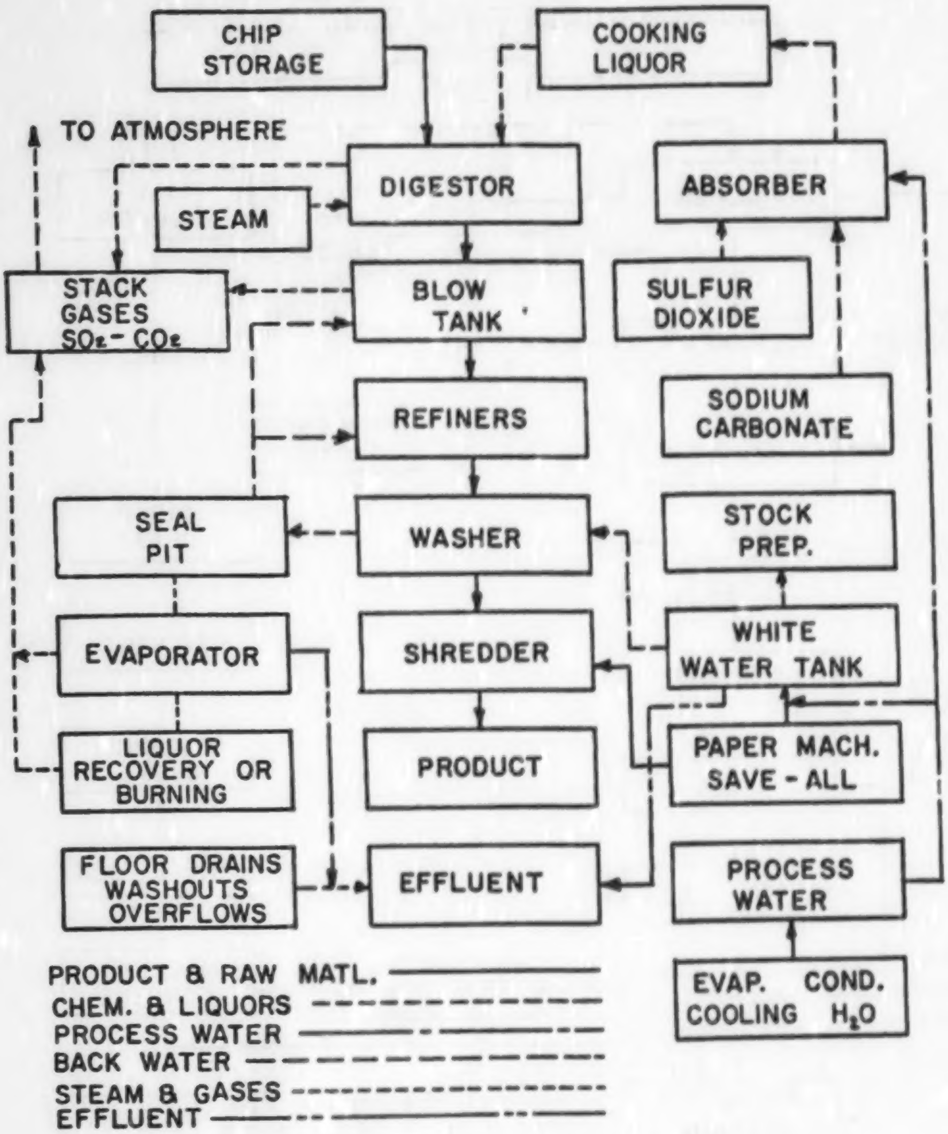

CHIP STORAGE
COOKING LIQUOR
TO ATMOSPHERE
DIGESTOR
ABSORBER
STEAM
STACK GASES SO_2 - CO_2
BLOW TANK
SULFUR DIOXIDE
REFINERS
SODIUM CARBONATE
SEAL PIT
WASHER
STOCK PREP.
EVAPORATOR
SHREDDER
WHITE WATER TANK
LIQUOR RECOVERY OR BURNING
PRODUCT
PAPER MACH. SAVE - ALL
FLOOR DRAINS WASHOUTS OVERFLOWS
EFFLUENT
PROCESS WATER
EVAP. COND. COOLING H_2O
PRODUCT & RAW MATL.
CHEM. & LIQUORS
PROCESS WATER
BACK WATER
STEAM & GASES
EFFLUENT

Figure 8-26-3
Pulp, Paper and Paperboard
Neutral Sulfite Semi-Chemical (NSSC)(B)

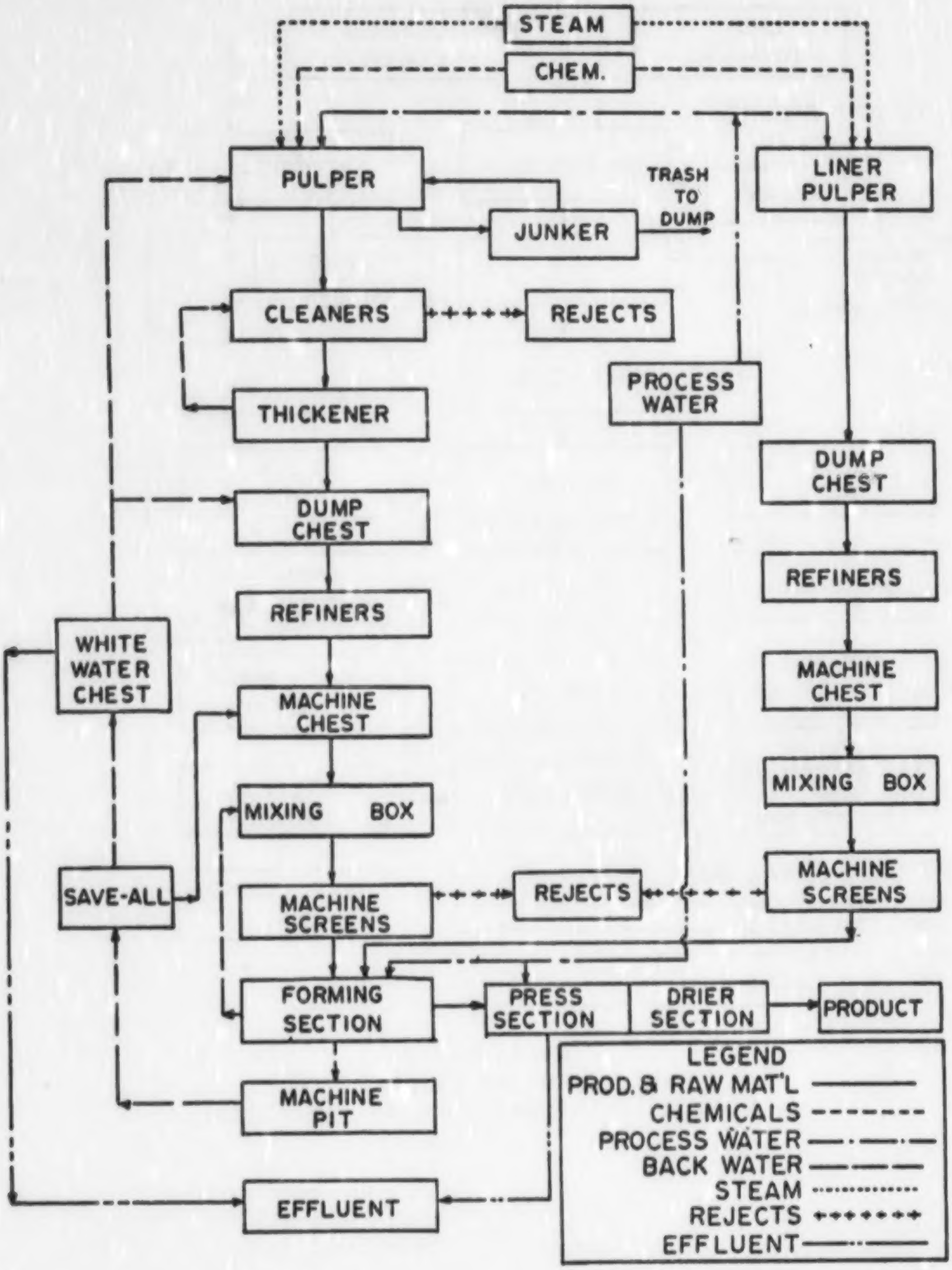

STEAM
CHEM.
PULPER
TRASH TO DUMP
LINER PULPER
JUNKER
CLEANERS
REJECTS
THICKENER
PROCESS WATER
DUMP CHEST
DUMP CHEST
REFINERS
REFINERS
WHITE WATER CHEST
MACHINE CHEST
MACHINE CHEST
MIXING BOX
MIXING BOX
SAVE-ALL
MACHINE SCREENS
REJECTS
MACHINE SCREENS
FORMING SECTION
PRESS SECTION
DRIER SECTION
PRODUCT
MACHINE PIT
EFFLUENT
LEGEND
PROD. & RAW MAT'L
CHEMICALS
PROCESS WATER
BACK WATER
STEAM
REJECTS
EFFLUENT

Figure 8-26-4
Pulp, Paper and Paperboard
Waste Paperboard Mill (E)

Groundwood

The energy used in producing conventional groundwood pulpstone or refiner is mechanical. Modified groundwood processes such as cold soda (chemi-mechanical) and chemi-groundwood methods employ a mild chemical treatment ahead of mechanical fiberizing. The latter processes are considered mechanical pulping because chemical pretreatment is much milder and the mechanical action more drastic than is the case in semichemical pulping. In thermo-mechanical pulping, an off-shoot of refiner groundwood, the pretreatment is accomplished with heat.

In the basic process, pulp is made by grinding logs, or short lengths of logs called billets, on a grindstone; pulp produced by passing wood chips through a disc refiner is termed refiner groundwood. In the chemi-groundwood process, the billets are first soaked or sprayed with a dilute solution of sodium sulfite before grinding; in cold soda (chemi-mechanical) pulping, chips are steeped in a caustic solution and refined. Such pretreatment softens the wood so that less power is required for grinding. In thermo-mechanical pulping, chips are first softened with heat and then refined under pressure.

Bleaching agents such as hydrosulfites and peroxides may be used in conjunction with mechanical pulping.

This pulp is used principally to manufacture newsprint, or other printing papers, molded fiber products, and "throw away" products (toweling, paper plates, tissues).

Wastewaters primarily contain BOD and suspended solids.

Chemical Pulping of Wood
Sulfite, Dissolving Sulfite, Bleached Kraft, Soda, Deinked

As the term implies, the energy utilized in chemical pulping to separate cellulose fibers from other wood components derives from chemical application. Wood is cooked in batch or continuous digesters, large pressure vessels, with solutions of various chemicals to the point at which non-cellulosic constitutents are dissolved and the fibers can be liberated by blowing the digester, or by jets of dilution water in the blow pit. Other than a simple "opener" device used in conjunction with the blowing of some high lignin content sulfite pulps, no subsequent mechanical devices are necessary.

Thus, chemical pulping methods are described as "full cook" processes. This differentiates them from the mechanical operations described above and semi-chemical pulping, which employ both chemical pretreatment and mechanical energy in varying relative degrees of strength.

Sulfite means the production of pulp, usually bleached, by a "full cook" process using an acidic cooking liquor of bisulfites of calcium, magnesium, ammonia, or sodium containing an excess of free sulphur dioxide. This pulp is used to manufacture a variety of paper products such as printing papers.

Dissolving Sulfite - Preparation of this pulp is similar to that discussed above. However, the wood is cooked at a higher than standard temperature. Cooking is continued until most of the lignin and part of the cellulose is dissolved. This pulp is used principally for the manufacture of rayon and other products requiring the virtual absence of lignin and a very high alpha-cellulose content.

Bleached Kraft means the production of bleached pulp by a "full cook" process utilizing a highly alkaline sodium hydroxide and sodium sulfide cooking liquor. This pulp is used to make a wide variety of papers and paperboards such as tissue, foodboard, and printing papers.

Also included in this subcategory is the production of highly bleached and purified kraft dissolving pulp utilizing a "precook" process. Kraft dissolving pulp is used principally for the manufacture of rayon and other products requiring the virtual absence of lignin and a very high alpha-cellulose content.

Soda means the production of bleached pulp by a "full cook" process utilizing a highly alkaline sodium hydroxide cooking liquor. This pulp is used principally to manufacture a wide variety of papers such as printing and writing papers.

Deinked means the production of pulp usually brightened or bleached from recycled waste papers in which an alkaline treatment is utilized to remove contaminants such as ink and coating pigments. The pulp is used, frequently in combination with chemical pulp, to manufacture a wide variety of papers such as printing, tissue, and newsprint.

Non-Integrated Processes (Fine, Tissue and Coarse Papers)

The term "Non-Integrated" means the manufacture of papers from wood or deinked pulp which has been prepared at another site. Only paper making occurs at the plant, and the paper making process has been described earlier.

4. Wastewater Characterization

Tables 8-26-1 and 8-26-2 contain wastewater characteristics for the industry.

Integrated pulp and paper mills generally operate continuously throughout the year except for the shutdowns for preventive maintenance and equipment repair and replacement. Modern practice is to employ continuous pulping processes; however, many mills are still using batch pulping processes which result in continuous discharges of wastewater with frequent surges. In addition, some older mills (generally relatively small, less than 100 tons/day)operate only 3 to 5 days per week.

The overall wastewater characteristics from wood pulping processes may vary seasonally because of the changes in characteristics of wood and other variations. The volume and characteristics of the process wastewater depend upon the degree of water reuse, chemical recovery systems, and the type and quality of paper involved.

The wastewaters generated from the paper and allied products industry contain BOD, COD, suspended solids, dissolved solids, color, acidity or alkalinity, and heat.

5. Control and Treatment Technology

In-Plant Control

Recyling, recovery and reuse of chemicals and fiber as well as good housekeeping can significantly reduce discharges. Substitution of dry barking for wet barking eliminates the waste flow from this process.

Normally the pulp is diluted to about 1% consistency to promote effective screening for the removal of knots and shives. The

TABLE 8-26-1
PULP AND PAPER INDUSTRY
RAW WASTEWATER CHARACTERIZATION

WASTE PARAMETER	SUBCATEGORIES											
	Unbleached Kraft-A	Sodium Base NSSC-B	Ammonia Base NSSC-C	Unbleached Kraft NSSC-D	Paper Board from Waste Paper-E	Groundwood	Sulfite	Dissolving Sulfite	Bleached Kraft	Soda	Deinked	Non-Integrated Plants
Flow Type	C	C	C	C	C	C	C	C	C	C	C	C
BOD (Mg/l)	200-500	1500-5000*	100-600	400-750*	60-100	300-3000*	750*-2000*	300-900*	150-300	200-600	300-500	100-300
TSS (Mg/l)	200-500	50-600	200-1000	150-750	100-5000	300-5000	150 -400	40-400	200-350	200-800	1000-2500	300-600
Color (Mg/l)	Present	Present	Present	Present	-	-	Present	Present	Present	Present	Present	Present
Heavy Metals	Present	Present	Present	Present	Present	Present	Present	Present	Present	Present	Present	Present
Oil & Grease	Present	Present	Present	Present	Present	Present	Present	Present	Present	Present	Present	Present

Note: *See Appendix 5 for parameters which may be inhibitory to biological systems
C - Continuous

TABLE 8-26-2
PULP AND PAPER INDUSTRY
RAW WASTEWATER CHARACTERIZATION
PRODUCTION BASED DATA

WASTE PARAMETER	SUBCATEGORIES											
	Unbleached Kraft-A	Sodium Base NSSC-B	Ammonia Base NSSC-C	Unbleached Kraft NSSC-D	Paper Board from Waste Paper-E	Groundwood	Sulfite	Dissolving Sulfite	Bleached Kraft	Soda	Deinked	Non-Integrated Plants
Flow (kl/kkg)[1]	40-100	20-100	20-100	40-80	5-50	8-17	60-200	230-350	40-110	80-125	55-100	80
Flow Type	C	C	C	C	C	C	C	C	C	C	C	C
BOD (kg/kkg)[2]	10-30	10-50	10-60	15-30	4-20	5-50	150	100-200	12-50	20-50	20-25	5-20
TSS (kg/kkg)[2]	10-40	4-30	-20	12-30	3-80	5-80	25	10-100	20-30	20-30	100-400	20-50

Note:

[1] kl/kkg - Kiloliters/1000 kg product produced

[2] kg/kkg - Kilograms/1000 kg product produced

C - Continuous

pulp is then rethickened on a decker for storage purposes. This operation accounts for about one third of the total BOD from a mill. If, after cooking, the pulp is passed through a fibrilizer which fractionates the knots remaining in the pulp, followed by a specially designed hot stock screen for removing the shives, the dilution step is eliminated. This practice reduces the amount of BOD discharged. Recycle of condensate streams instead of using new makeup water in plant operations reduces the wastewater flow.

A rule of thumb sometimes used in this industry is that one third of the BOD and TSS in the raw waste is due to spills, overflows, and wash-ups which occur when the production process is not in equilibrium. These losses occur due to a variety of factors including breakdown of equipment, routine maintenance, planned shutdowns and startups, power failures, and grade changes. These can be avoided by the use of the following techniques:
1) Evaporators should be periodically "boiled out" to remove scale and other substances, and the flushed material stored and returned to the mill processes.
2) Storage facilities can be used to store overflows from operations during upset conditions, and then returned to the process.
3) Continuous monitoring can be used to give immediate warning to plant upsets.

Many mills use a save-all to recover fibrous material escaping from the paper machine. This reduces the waste load.

Treatment Technology

Suspended solids can be reduced by mechanical clarifiers, flotation units or sedimentation lagoons.

BOD reduction is generally accomplished by biological means, including oxidation basins, aerated stabilization basins, and the activated sludge process.

Color removal is accomplished by lime treatment with clarification, coagulation with alum and ferric chloride and activated carbon.

Refer to Table 8-26-3 for removal efficiencies for the various processes.

TABLE 8-26-3
PULP AND PAPER INDUSTRY
WASTEPAPER TREATMENT PRACTICES

Pollutant and Method	Removal Efficiencies Percent
TSS	
Mechanical Clarifiers	Up to 95%
Dissolved Air Flotation	Up to 98%
BOD	
Biological Treatment	85 - 99 %
COLOR	
Lime Treatment	74 - 91
Coagulation with Aluminum and Ferric Chloride	80 - 90
Activated Carbon	70

BUILDER'S PAPER AND ROOFING FELT

1. General Industry Description

This industry manufactures heavy papers for the construction industry from varying combinations of wood, waste paper and/or rags. Establishments engaged in this industry are covered by Standard Industrial Classification (SIC) 2661.

2. Industrial Categorization

Since both Builder's Paper and Roofing Felt are similarly processed, they constitute one discrete category.

3. Process Description

Building papers are generally characterized as saturating papers, flooring paper, and deadening paper which are used in the construction and automotive industries. They differ from unsaturated roofing felts only in thickness and possible chemical additives added to the process in order to achieve a specific property. The function of dry roofing felt is to provide a strong, highly absorbent material as a backing for the coatings which provide the characteristics desired in the finished product, i.e. water repellancy, weather & heat resistance, and strength.

A flow diagram for the industry is shown in Figure 8-27-1.

The manufacture of building paper involves three processes:

1. Stock preparation area
2. Wet end of machine
3. Dry end of machine

(1) Stock Preparation Area

Raw materials including waste paper, defibrinated wood, wood flour, pulp mill rejects, rags, wood chips, and sawdust are prepared for use. Wood chips are pulped,occasionally preceded by a steaming process. Rags & waste paper are cut, shredded, pulped and mixed with water. The various stock components are blended, and stored in a machine stock chest.

(2) Wet End Area

The stock is pumped from the stock chest through a cylinder wire where fibers are retained and a sheet is formed. The water passes through the wire and is recycled.

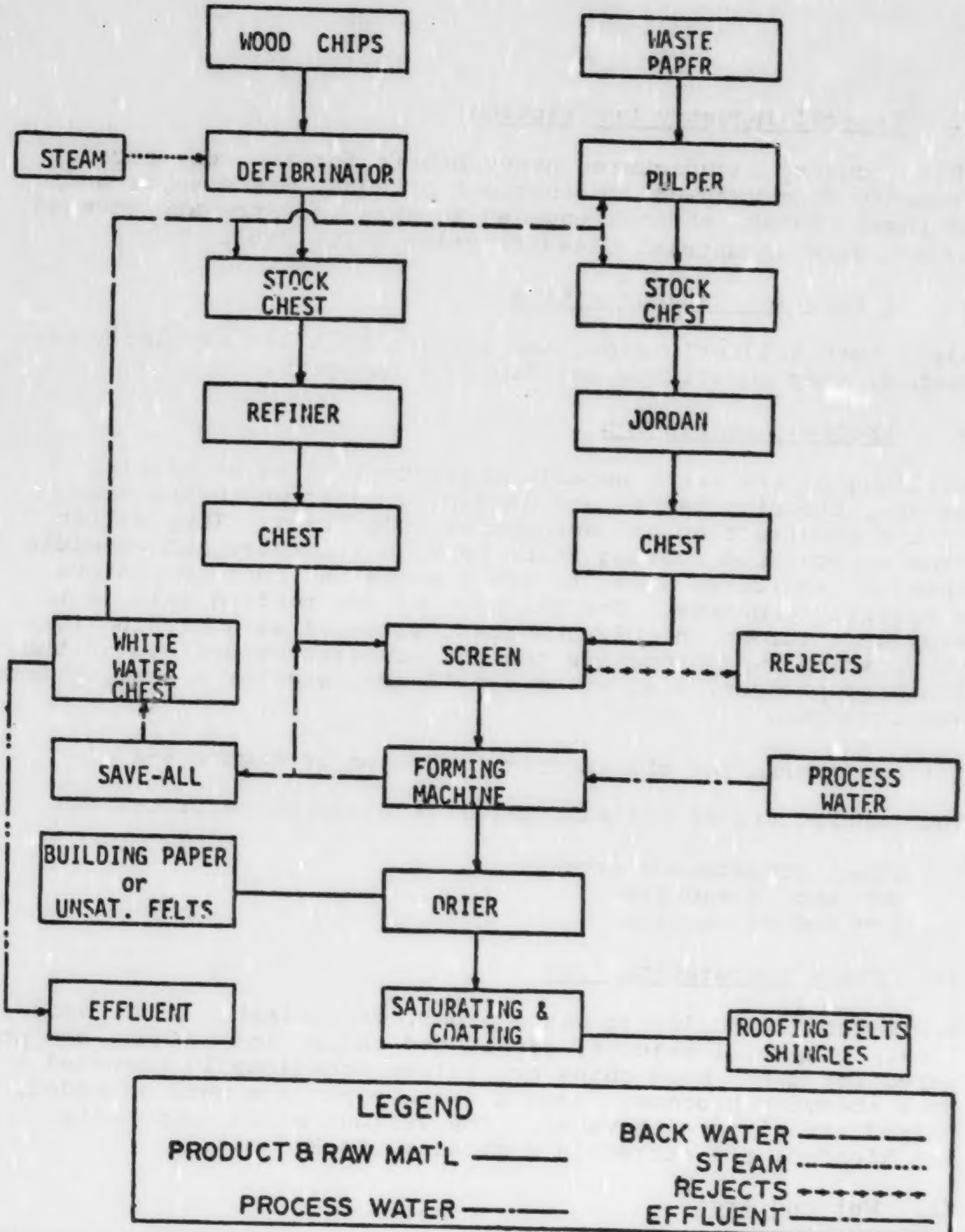

WOOD CHIPS
WASTE PAPER
STEAM
DEFIBRINATOR
PULPER
STOCK CHEST
STOCK CHEST
REFINER
JORDAN
CHEST
CHEST
WHITE WATER CHEST
SCREEN
REJECTS
SAVE-ALL
FORMING MACHINE
PROCESS WATER
BUILDING PAPER or UNSAT. FELTS
DRIER
EFFLUENT
SATURATING & COATING
ROOFING FELTS SHINGLES
LEGEND
PRODUCT & RAW MAT'L
PROCESS WATER
BACK WATER
STEAM
REJECTS
EFFLUENT

FIGURE 8-27-1
BUILDING PAPER AND ROOFING
FELT PROCESS DIAGRAM

(3) Dry End Area

The sheet passes through the dryer section. This building paper may be the final product or it may be subject to additional processing to produce roofing felt.

Saturating and Coating - The paper may be saturated with asphalt and coated with talc. Cooling water is supplied after each saturation generating a wastewater. The saturated felt may be subjected to a coating of granular stone and/or mica. These particles fall to the floor and are washed to the sewer. This wastewater represents a principal source of inert suspended solids.

4. Wastewater Characterization

Table 8-27-1 shows the raw waste loadings for the industry.

5. Control and Treatment Technology

In-Plant Control - Large quantities of water are necessary to form a sheet of paper. In recent years very extensive recycling has been achieved by the industry. One mill reports a completely closed process water system with no discharge to the environment using the activated sludge process.

Most mills employ a save-all or filtration system to recover fibrous and other suspended solids. High pressure low volume showers for cleaning purposes reduces water use. Cooling towers are utilized to control thermal discharges and make cooling water suitable for reuse.

Treatment Technology - The dissolved organic components of cellulosic products as well as adhesives, sizing materials and resinates present in the waste load are amenable to biological treatment.

TABLE 8-27-1
RAW WASTEWATER CHARACTERISTICS
BUILDERS PAPER AND ROOFING FELT

Parameter		Concentration
Flow Range	(l/1000 kg)	4,200/54,000
BOD	(kg/1000 kg)[1]	7/13
TSS	(kg/1000 kg)[1]	4/42
BOD	(mg/l)	130-3,000*
TSS	(mg/l)	75-10,000

Note:

(1) kg/1000 kg and l/1000 kg is based on product produced (lower limit/upper limit)

* See Appendix 5 for parameters which may be inhibitory to biological systems.

1. General Industry Description

Meat packing plants carry out slaughtering and processing of cattle, calves, hogs, and sheep for the preparation of meat products and by-products. Meat processing plants purchase animal carcasses, meat parts, and other materials and manufacture sausages, cooked meats, cured meats, smoked meats, canned meats, frozen and fresh meat cuts, natural sausage casings, and other specialties.

Establishments engaged in the meat slaughtering processing industry are included in Standard Industrial Classifications (SIC) 2011, 2013, 2032, 2077.

2. Industrial Categorization

Industrial Categorization	Designation
Simple Slaughterhouses	A
Complex Slaughterhouses	B
Low-Processing Packinghouses	C
High-Processing Packinghouses	D
Small Processor	E
Meat Cutter	F
Sausage and Luncheon Meats Processor	G
Ham Processor	H
Meat Canner	I
Renderer	J

3. Process Description

Figure 8-28-1 is a process flow diagram for the meat industry that shows the various processes described below.

Simple Slaughterhouse (A) A slaugherhouse is a plant that slaughters animals and has as its main product fresh meat as whole, half or quarter carcasses or smaller meat cuts. A slaughterhouse includes the following operations:

Livestock Pens - Contain the animals while waiting their turn for slaughter. Wastewater results from watering troughs, washdowns, urine and runoff if the pen is not covered.

Slaughtering - The slaughtering of animals includes the killing and hide removal in the case of cattle, calves and sheep; and scalding and dehairing for hogs; eviscerating; washing of the carcasses and cooling.

The blood, hides, hair and viscera are subject to further processing. A slaughterhouse which is subcategorized as "simple" may send these by-products out for further processing or may engage in only one or two of these by-product processing operations:

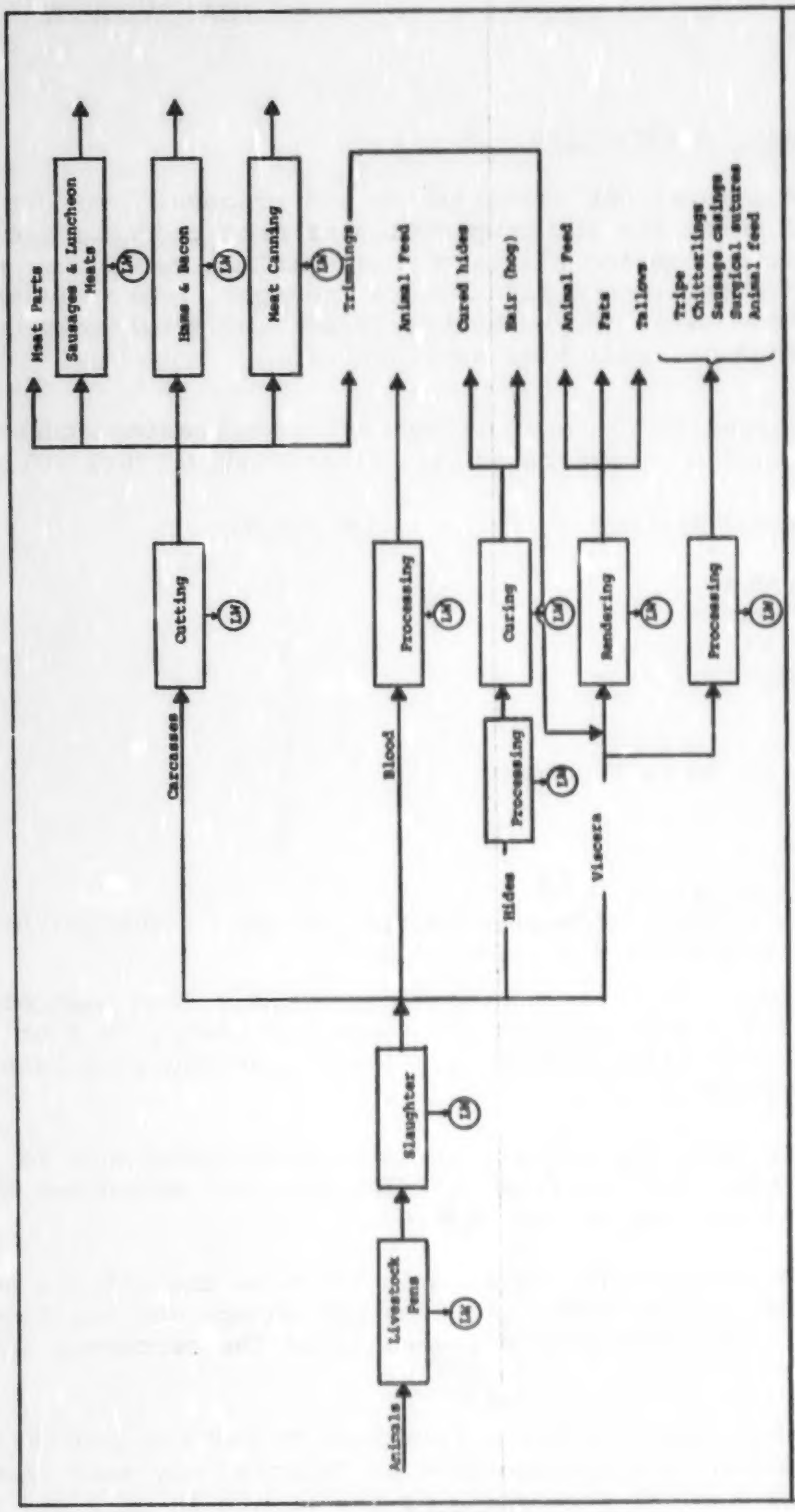

Animals
Livestock Pens
LW
Slaughter
LW
Carcasses
Cutting
LW
Meat Parts
Sausages & Luncheon Meats
LW
Hams & Bacon
LW
Meat Canning
LW
Trimmings
Blood
Processing
LW
Animal Feed
Hides
Processing
LW
Curing
LW
Cured hides
Hair (hog)
Viscera
Rendering
LW
Animal Feed
Fats
Tallows
Processing
LW
Tripe
Chitterlings
Sausage casings
Surgical sutures
Animal feed

FIGURE 8-28-1
MEAT INDUSTRY

By-Product Operations

(1) Blood Processing - The blood may be heated to coagulate the albumin; then the albumin and fibrin are separated for further processing into pharmaceutical preparations. The blood water may be evaporated for animal feed or it may be discharged. In most cases, the whole blood is sent directly to conventional blood dryers and used for animal feed.

(2) Viscera Handling - The contents of the paunches, 50 to 70 pounds of partially digested feed, may be washed out with water and passed over a screen. The separated solids go to solid waste handling. The liquor is generally sewered. The paunch contents are sometimes dumped on the screen without the use of water and are dried and removed. In some plants the entire paunch contents are sewered. The paunch is washed thoroughly if it is to be used for edible products.

Intestines may be sent directly to rendering or they may be hashed and washed and then sent to rendering. Paunches, stomachs and intestines can be marketed as tripe, chitterlings, sausage casings, surgical sutures, mink or pet food. Viscera handling results in stomach contents, intestines, and considerable grease being discharged in the wastewater.

(3) Hide Processing - Hides may be processed wet or dry. Wet processing involves hide demanuring, washing and defleshing, followed by a brine cure in a brine vat or raceway. In dry curing, the washed defleshed hides are packed with salt and stacked in the curing room. Hide processing leads to significant loads of blood, tissue, dirt and salt in the wastewater.

(4) Cutting - In the cutting area carcasses are cut for marketing or for further processing. The trimmings may be used for sausage and canning, or for rendering of fats and tallows. Much of the meat, bone, dust, fat, tissues, and blood is discharged during clean-up.

(5) Rendering separates fats and water from tissue. Inedible rendering utilizes bones, offal, condemned animals and is used in animal feed. The materials are passed through a grinder and rendered by one of three methods: wet, dry, or low temperature.

In the wet rendering process the ground trimmings are pressure cooked. The fat phase is separated, the solids are screened out, and the tankwater is evaporated to a thick protein-rich material known as "stick" which is added to animal feed.

In dry rendering the most widely used process, the material is cooked until the moisture is driven off. The cooked material is screened to remove the fat from the solid proteinaceous residue.

In low temperature rendering the finely ground material is heated to just above the melting point of the fat. The fat is separated by centrifugation.

Spills and discharges from washdown further contribute to wastewater discharges.

Grease recovery operations effectively remove pollutants and recover valuable by-products.

Complex Slaughterhouse (B) A slaughterhouse that does extensive by-product processing, usually including at least three of the by-product operations discussed in (A) is subcategorized as "complex".

Low-Processing Packinghouse (C) A packinghouse is a plant that both slaughters and processes fresh meat to cured, smoked, canned, and other meat products. A packinghouse that is subcategorized as "Low Processing" is one that processes no more than the total animals killed at that plant, normally processing less than the total kill. The processed meat products for this subcategory are limited to: chopped beef, meat stew, canned meats, bacon, hams, franks, wieners, bologna, hamburger, luncheon meat loaves, and sausages.

High-Processing Packinghouse (D) A packinghouse which includes all the processes described in (C) but processes all animals slaughtered at the site plus additional carcasses from outside sources is subcategorized as "High-Processing."

Meat processors (E-I) purchase animal carcasses, meat parts and other materials in either a fresh or frozen state and manufacture sausages, cooked meats, cured meats, smoked meats, canned meats, frozen and fresh meat cuts, natural sausage casings and other prepared meats and meat specialties.

The frozen raw materials are handled in one of three ways:

1. Wet thawing
2. Dry thawing
3. Chipping

Frozen materials that are wet thawed are submerged in tanks containing warm water. This process generates a large volume of wastewater.

The other two thawing methods generate wastewater from clean-ups. In dry thawing the meat is allowed sufficient time to thaw. Chipping involves size reduction equipment designed to handle frozen meat.

Small Processor (E) The small processor is one which produces 6,000 lb. (2730 kg) or less of finished product per day of any type or combination of finished meat products.

Meat Cutter (F) Meat cuts and portion controlled products are prepared for hotels, restaurants, institutions and fast food outlets.

Sausage and Luncheon Meats (G) These are comminuted meat products which require substantial size reduction, intensive mixing, and usually the molding or forming of the finished product.

Ham Processor (H) The production of hams and bacon, involves the preparation of the raw material for the injection or application of a pickle solution followed by cooking and smoking. The products are then cooled, aged if desired, sliced and packaged.

Meat Canner (I) Can filling is a highly mechanized high-speed operation. This operation results in a substantial quantity of wastewater from spills and from frequent equipment wash-ups. The pressurized cooking of canned meat products does not generate a waste load.

Renderer (J) The renderer as covered in this subcategory consists of both the offsite or independent renderer and the on-site or captive renderer. The independent renderer reprocesses discarded animal materials such as fats, bones, hides, feathers, blood, and offal into saleable by-products, almost all of which are not suitable for human consumption. Also processed are "demo stock", which are whole animals that die by accident or through natural causes. A captive renderer is housed on the same premises as the meat processing plant and conducts its business as an adjunct to the meat processing operation. Products include edible lard and tallows made from animal fats, in addition to providing inedible by-products.

4. Wastewater Characteristics

Wastewater characteristics are shown in Table 8-28-1 and 8-28-2. The meat industry is a year round operation with daily operation on an intermittent basis. Plants usually shut down daily for extensive cleanups.

5. Control and Treatment Technology

The wasteload discharged from the meat industry can be reduced to desired levels, including no-discharge of pollutants, by conscientious wastewater management, in-plant waste controls, process revisions, and by the use of primary, secondary, and tertiary wastewater treatment. Figure 8-28-2 is a schematic of a possible waste reduction program to achieve high removal of pollutants.

In-Plant Control

Livestock holding pens may be covered and dry cleaned with only periodic washdown. Solid wastes may be disposed of on farm land as fertilizer. A separate sewer and manure pit may be provided for liquid wastes. Disposal may be on land or to secondary treatment systems.

Blood Handling - Blood may be totally contained and collected, and water use avoided in the blood handling system.

Water from washups can be minimized and drained into the blood collection system. Bloodwater can be avoided by installing a blood dryer or it can be rendered, evaporated, or mixed with paunch and cooked to produce a feed material. Since blood has a high BOD5 value and can generally be recovered, discharge of blood directly to POTW's should be avoided.

Paunch Handling - Paunch contents need not be washed out. Dumping the contents followed by high pressure but minimal water rinse minimizes the wasteload from this operation. Vacuuming the contents can also be considered. Liquids screened from the paunch material can be collected and evaporated or rendered. Consideration may be given to transporting the entire unopened paunch to rendering. In any event, the discharge of paunch manure to POTW collection systems should be avoided if possible.

Viscera Handling - Inedible viscera can be rendered without washing.

Slaughtering - Troughs under the killing floor are very effective in collecting and containing blood and solids.

Rendering - The water centrifuged from this process can be sold as 50-60% edible stickwater instead of discharging. Tankwater from wet rendering has a BOD_5 range of from 22,000 - 45,000 mg/l. It can be evaporated and blended into animal feed.

TABLE 8-28-1
MEAT PRODUCTS INDUSTRY
RAW WASTEWATER CHARACTERISTICS

	Simple Slaughterhouse A	Complex Slaughterhouse B	Low Processing Packinghouse C	High Processing Packinghouse D	Small Processor E	Meat Cutter F	Sausage and Luncheon Meats G	Ham Processor H	Meat Canner I
Flow Range (GPD)	7M-2.14MM	148M-4.9MM	50M-6.2MM	10M-6.6MM	3-15M	300-152M	1000-1.56MM	270-1.7MM	27,600-1.097MM
Average Flow (GPD)	300M	1.16MM	900M	1.16MM	840	9940	120,800	92,700	240,300
Flow Type	B	B	B	B	B	B	B	B	B
BOD Range (Mg/1)	500-1400*	500-1400*	500-1400*	500-1400*	500-1400*	500-1400*	500-1400*	500-1400*	500-1400*
Average BOD (Mg/1)	1100	1500	1000	1300	1000	875*	275	525	1000*
TSS (Avg) (Mg/1)	1050	1300	750	850	250	1100	360	300	400
TSS (Range)(Mg/1)	70-1500	70-1500	70-1500	70-1500	70-1500	70-1500	70-1500	70-1500	70-1500
TDS (Mg/1)	500-2500 *	500-2500 *	500-2500 *	500-2500*	550	400-1200*	1300*	3000*	2000*
COD (Mg/1)	290-4600*	290-4600*	290-4600*	290-4600*	560	480	480	1200*	2500*
pH	6.5-8.5	6.5-8.5	6.5-8.5	6.5-8.5	6.5-8.5	6.5-8.5	6.5-8.5	6.5-8.5	6.5-8.5
Color	High	High	High	High	High	High	High	High	High
Grease (Mg/1)	400*	800*	400*	700*	150*	200*	125*	225*	185*
Phosphorus (Mg/1)	9.4	45	17	30	70	8	20	28	80
Kjeldal N(Mg/1)	128	114	68	105	200	5	25	20	40
Ammonia (Mg/1)	7-50	7-50	7-50	7-50	68	1	1.5	1.5	6
Nitrates (Mg/1)	.02-4.5	.02-4.5	.02-4.5	.02-4.5	11.8	.88	1.14	2.07	.04
Nitrites (Mg/1)	.02-4.5	.02-4.5	.02-4.5	.02-4.5	2.1	.04	.3	.82	.14
Chlorides (Mg/1)	488	380	460	1246*	1060*	162	464	758	13.5-138
Total Coliform (million/100 ml)	.5-60	.5-60	.5-60	.5-60	.5-60	46.5	.5-60	22	.56
Fecal Coliform (million/100 ml)	.012-1.6	.012-1.6	.012-1.6	.012-1.6	.6	.44	.012-1.6	.38	.012
Temperature (^{o}C)	27-38	27-38	27-38	27-38	27-38	87-38	27-38	27-38	27-38

Note: *See Appendix 5 for parameters which may be inhibitory to biological treatment systems

B - Batch Operation
M - 1000
MM - 1,000,000

Table 8-28-2
MEAT PRODUCTS INDUSTRY
RAW WASTE CHARACTERISTICS BASED ON PRODUCTION

Parameter	Simple Slaughterhouse A	Complex Slaughterhouse B	Low Processing Packinghouse C	High Processing Packinghouse D	Small Processor E	Meat Cutter F	Sausage & Luncheon Meats G	Ham Processor H	Meat Canner I
Flow Range (1/kkg)[1]	1334/14641	3627/12507	2018/17000	5444/20261	83/25000	175/3635	1084/26100	288/29200	3170/20375
Flow (Average)(1/kkg)	5,328	7,379	7,842	12,514					
BOD Range (kg/kkg)[2]	1.5/14/3	5.4/18.8	2.3/18.4	6.2/30.5	.99/1.1	.23/1.09	.5/5.4	.24/16.2	.8/24
BOD (Average)(kg/kkg)	6.0	10.9	8.1	16.1					
SS Range (kg/kkg)	.6/12.9	2.8/20.5	.6/13.9	1.7/22.5	.73/.86	.34/.94	.12/12	.15/9.45	.46/11.5
SS (Average)(kg/kkg)	5.6	9.6	5.9	10.5					

[1] liters/1000 kilograms live weight killed (lower limit/upper limit)

[2] kg/1000 kilograms live weight killed (lower limit/upper limit)

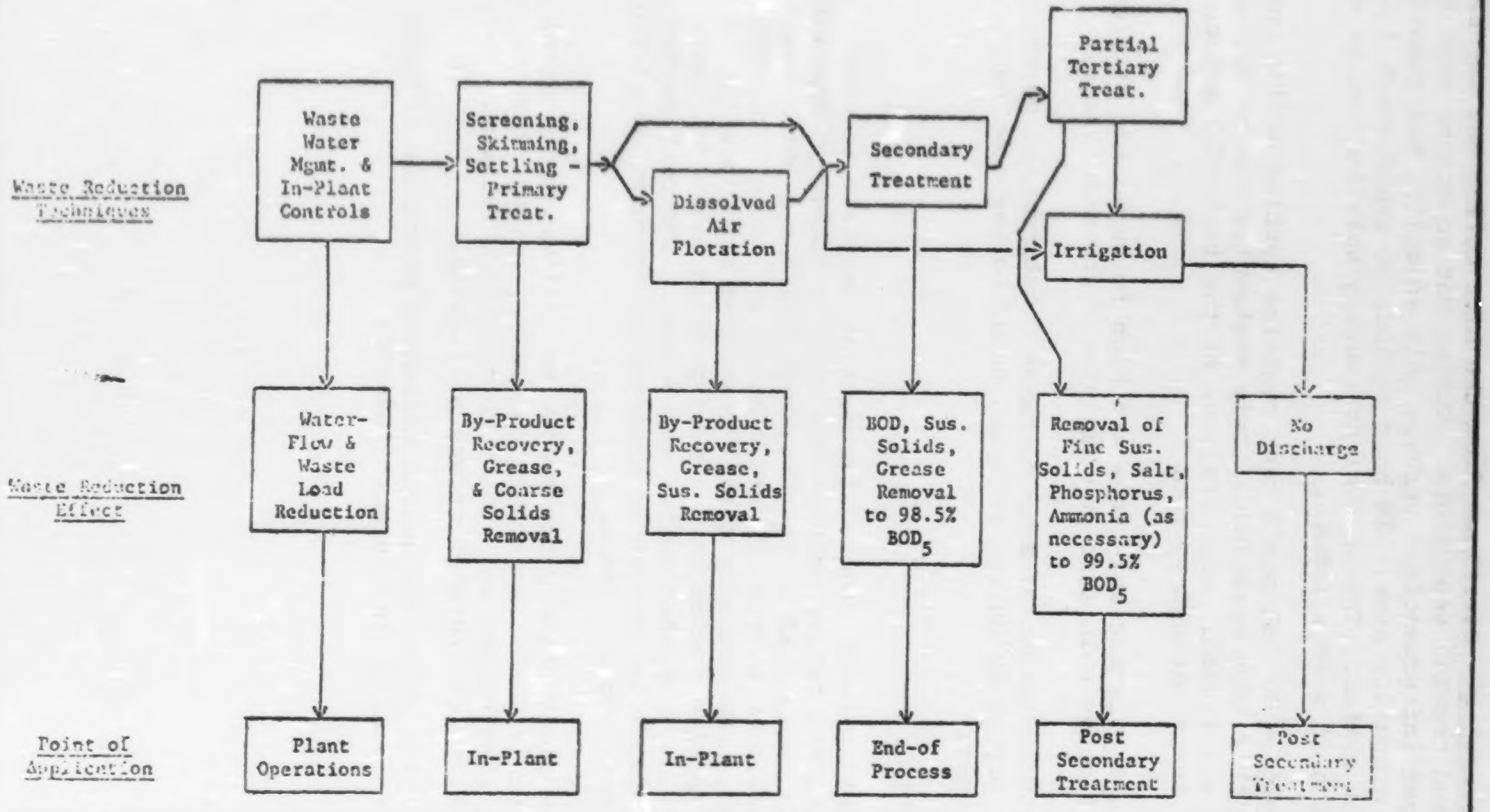

Waste Reduction Techniques
Waste Reduction Effect
Point of Application
Waste Water Mgmt. & In-Plant Controls
Screening, Skimming, Settling - Primary Treat.
Dissolved Air Flotation
Secondary Treatment
Partial Tertiary Treat.
Irrigation
Water-Flow & Waste Load Reduction
By-Product Recovery, Grease, & Coarse Solids Removal
By-Product Recovery, Grease, Sus. Solids Removal
BOD, Sus. Solids, Grease Removal to 98.5% BOD5
Removal of Fine Sus. Solids, Salt, Phosphorus, Ammonia (as necessary) to 99.5% BOD5
No Discharge
Plant Operations
In-Plant
In-Plant
End-of Process
Post Secondary Treatment
Post Secondary Treatment

Figure 8-28-2 Meat Industry Waste Reduction Program

Hide Processing - Overflows from the hide curing vat may be contained and treated separately. Curing vat solutions high in salt are dumped infrequently - perhaps only annually, but should be drained gradually over a 24 hour period, to avoid shock load to the treatment system. The life of the curing solution can be extended by pumping it over a screen.

Scald Tank - The hog scald tank contains settled solids and wastewater with a high wasteload. This wastewater can be collected, treated and reused. Slow drainage of the tank will reduce shock load on the treatment system.

Pickling and Curing solutions are high in sugar and salt content. Reuse of these solutions can minimize wastewater loads.

Plant and equipment cleanup consumes a substantial quantity of water. Dry cleaning and scraping prior to washdown can minimize waste loads.

Treatment

Equalization tanks reduce fluctuations in waste streams. Static, vibrating and rotary screens are used to intercept the solids, thus reducing waste load to the treatment plant. A catch basin equipped with a skimmer to remove grease and scum, and a scraper to remove the sludge are commonly used. Dissolved air flotation is the single most effective device that a meat packing plant can install to remove fine suspended solids and grease. Improved performance of the air flotation system is achieved by coagulation of the suspended matter prior to treatment.

After in-plant primary treatment, the following biological systems are commonly used: anaerobic processes, aerobic lagoons, variations of activated sludge and high rate trickling filters. Tertiary treatment systems can further reduce pollutants.

Table 8-28-3 shows wastewater treatment practices and the per cent removals obtained in the meat industry.

Table 8-28-3
Meat Industry
Wastewater Treatment Practices

Treatment System	Use	Effluent Reduction
Dissolved air flotation (DAF)	Primary treatment or by-product recovery	Grease, 60% removal, to 100 to 200 mg/l BOD$_5$, 30% removal SS, 30% removal
DAF with pH control and flocculants added	Primary treatment or by-product recovery	Grease, 95-99% removal, BOD$_5$, 90% removal SS, 98% removal
Anaerobic + aerobic lagoons	Secondary treatment	BOD$_5$, 95% removal
Anaerobic + aerated + aerobic lagoons	Secondary treatment	BOD$_5$, to 99% removal
Anaerobic contact process	Secondary treatment	BOD$_5$, 90-95% removal
Activated sludge	Secondary treatment	BOD$_5$, 90-95% removal
Extended aeration	Secondary treatment	BOD$_5$, 95% removal
Anaerobic lagoons + rotating biological contactor	Secondary treatment	BOD$_5$, 90-95% removal
Chlorination	Finish and disinfection	--
Sand filter,	Tertiary treatment & Secondary treatment	BOD$_5$, to 5-10 mg/l SS, to 3-8 mg/l
Microstrainer	Tertiary treatment	BOD$_5$, to 10-20 mg/l SS, to 10-15 mg/l
Electrodialysis	Tertiary treatment	TDS, 90% removal
Ion exchange	Tertiary treatment	Salt, 90% removal
Ammonia stripping	Tertiary treatment	90-95% removal
Carbon adsorption	Tertiary treatment	BOD$_5$, to 98% removal as colloidal & dissolved organic
Chemical precipitation	Tertiary treatment	Phosphorus, 85-95% removal, to 0.5 mg/l or less
Reverse osmosis	Tertiary treatment	Salt, to 5 mg/l TDS, to 20 mg/l
Spray irrigation	No discharge	Total
Flood irrigation	No discharge	Total
Ponding and evaporation	No discharge	Total

1. General Industry Description

The water supply industry treats and distributes water for domestic, commercial, and industrial use. This industry does not distribute water for irrigation. Operations include: coagulation, softening, iron and manganese removal, aeration, disinfection and fluoridation.

This industry is delineated by Standard Industrial Classification (SIC) 4941.

2. Industrial Categorization

Subcategory I - Plants that use only coagulation, oxidative iron and manganese removal, direct filtration, or diatomaceous-earth filtration. Only one of the above solids-removal processes is used. Plants with combinations of two or more solids-removal processes are included in other subcategories.

Subcategory II - Plants that use the lime or lime-soda softening processes.

Subcategory III - Plants that use combinations of coagulation and chemical softening, or oxidative iron-and-manganese removal and chemical softening.

Zeolite softening, dissolved solids removal, and defluoridation processes have not been subcategorized since treatment of their wastes have not be adequately demonstrated on a commercial basis.

3. Process Description

The purpose of a water treatment plant is to remove or inactivate constituents in the water that are undesirable for the intended use. Constituents that might be removed in water treatment plants include suspended solids, pathogens, colloids, iron and manganese, ions that cause hardness, and materials that impart color, odor, or taste. Treatment plants that are only required to remove one of the above are generally simple, while treatment plants that must remove two or more of the above constituents contain many different unit processes.

Presedimentation - Presedimentation is used with raw waters that contain relatively high concentrations of easily settled suspended solids, such as sand or silt. The treatment process consists of settling tanks with large enough detention time to allow the solids to settle out. Wastes from this process consist of sludges of up to 20% settled solids.

Coagulation - Coagulation is used to aid in sedimentation when suspended particles are not readily settleable. Coagulation (with flocculation) causes the particles to collide and agglomerate, forming larger particles which can be easily clarified from the solution. Materials used as coagulants include polyelectrolytes and metal salts, such as aluminum sulfate and ferrous sulfate. Sodium aluminate and lime are also used when pH adjustment is desired. Wastes from these operations are sludges containing the suspended solids removed, plus the coagulants added. The sludges are hard to dewater, and are generally less than 2% solids.

Softening - Softening processes used to reduce the concentration of substances that cause hardness in water (calcium and magnesium) are of two types: chemical and zeolite. Chemical softening consists of the use of lime to precipitate calcium carbonate and magnesium hydroxide. Since lime alone does not remove all of the hardness, soda ash may be used to further reduce hardness. If iron and manganese are present they may also be removed in the softening process. The unit operations or chemical softening include chemical addition, rapid mixing, flocculation, and clarification.

Zeolite softening is an ion exchange process. Natural or synthetic "resins" have the capacity of exchanging ions in their matrix with ions in solution. When the right resin is selected, only ions associated with hardness (calcium and magnesium) are removed from solution. When the resins have been in operation for a period of time (6-24 hours) the resin becomes exhausted, and must be regenerated. This regeneration waste stream is a concentrated brine containing salts of calcium and magnesium.

Iron and Manganese Removal - Although iron and manganese are removed in the lime softening operation, many plants need to remove iron and manganese, but do not need to soften their water. In these cases, iron and manganese are removed by oxidation (aeration) and filtration. The oxidation step can also be accomplished with chlorine and potassium permanganate. If the pH is too low for the precipitation of iron and manganese, lime is added for pH adjustment. Wastes from this operation consist of filter backwashes, which contain iron and manganese salts, and are high in color.

Filtration - Filtration is usually the final step in removing solids regardless of the processes preceding the filtration step. Filtration is used to remove silt, sand, colloids, viruses, algae, bacteria, clay particles, etc. There are several types of filters used; the most widely used is the rapid sand filter. This filter consists of a support medium of gravel followed by a layer of carefully sized sand. Filters can be either of the pressure or gravity type. Wastes from filtration consist of backwashes, which contain the particles removed by the filter, at concentrations of 10 to 100 times their concentration in the raw water.

Dissolved Solids Removal - Processes for removal of dissolved solids include electrodialysis, reverse osmosis, and distillation. Electrodialysis is a process in which many membranes are arranged parallel to each other to form solution compartments held between a pair of electrodes. The feed water flows through every other solution compartment. When a voltage is applied to the electrodes, electrolytic solids in the feed water are transported across the membranes into a waste-brine stream flowing between the solution compartments that contain feed.

Reverse osmosis is a pressure-operated process in which special membranes permit water to pass through but block impurities. Distillation consists of vaporizing the water in the feed solution and recondensing the pure water vapor. Wastes from these three processes contain concentrated brine solutions.

4. Wastewater Characterization

Table 8-29-1 shows the waste characteristics for the processes described above.

TABLE 8-29-1

THE WATER SUPPLY INDUSTRY
RAW WASTEWATER CHARACTERISTICS

Waste Parameter (mg/l)	Process						
	Presedimentation (sludge)	Coagulation (sludge)	Chemical Softening	Zeolite Softening	Iron and Manganese Removal	Filtration	Dissolved Solids Removal
Flow Type	C & B	C & B	C & B	B	B	B	C
BOD	30-300	30-300	30-300	Present	Present	30-300	Present
TSS	10M-200M	2M-20M	10M-100M	Nil	1M	1M	Nil
TDS	50-4M*	50-4M*	50-4M*	10M*-40M*	50-4M*	50-4M*	10M*-40M*
COD	30-3M*	30-3M*	30-3M*	Present	Present	30-3M*	Present
pH	6-9	6-9	7-11*	6-9	6-9	6-9	6-9
Color	Present	Present	Present	Present	Present	Present	Present
Iron	Present	Present	Present	Present	Present	Present	Present
Manganese	Present	Present	Present	Present	Present	Present	Present
Fluoride	0.01-3	0.01-3	0.01-3	Greater than 10	0.01-3	0.01-3	0.01-3

otes:

M = 1,000
MM = 1,000,000
* - See Appendix 5 for parameters which may be inhibitory to biological systems
B - Batch Operated
C - Continuously Operated

5. Control and Treatment Technology

In-Plant Control

Many plants use more chemicals than are required to reach the desired effluent quality. The use of laboratory tests to guide the plant operator in his dosage of chemicals can reduce the amount of chemical added, and therefore reduce the pollutant load of the waste from the plant.

The use of organic polymers in place of inorganic coagulants reduces the amount of waste solids generated, and produces a sludge that is more easily dewatered. In addition, the polymers are biodegradable.

Recycling of filter backwash can greatly reduce the amount of wastewater produced by a water treatment plant. Since filter backwashes are low in solids compared to sludges, recycling of the backwash water to the head end of the plant, and letting the initial clarifier remove the suspended solids from the backwash water eliminates a waste stream. The backwash water should be placed in a detention tank and bled slowly to the head end of the plant. This detention tank can also be used for clarifying the backwash water.

Chemical recovery can also be used as an in-plant control measure. Alum can be recovered by thickening the alum sludge to greater than 2% solids, adding sulfuric acid to dissolve the aluminum, dewatering of the sludge which recovers the aluminum as alum, and then reusing the alum.

Lime is recovered by burning the calcium carbonate sludge from the lime softening clarifier in a furnace, which produces calcium oxide. Calcium oxide is then slaked in water,producing lime. Magnesium hydroxide must be removed before the burning process.

Treatment Technology

The sludges may be handled by equalization and storage. This can be accomplished by thickening of the sludge, which reduces its volume. Thickening prior to sludge dewatering reduces the size of the sludge dewatering equipment.

Prior to sludge dewatering, sludge conditioning with organic polymers is generally practiced in order to aid in the dewatering step. Dewatering systems include lagoons, vacuum filtration, filter presses, and centrifuges. Lagoons are the most popular and the cheapest to run, but require large land areas.

MISCELLANEOUS FOODS AND BEVERAGES

1. General Industry Description

This industry includes establishments engaged in the manufacture of vegetable oils, beverages (alcoholic and non-alcoholic), bakery and confectionary products, pet foods and miscellaneous specialty food products. The general category includes approximately 10 percent of U. S. industry and 60 percent of the food processing industry in terms of number of industrial establishments.

In general, wastes from this industry are non-toxic, biodegradable and amenable to standard sewage treatment processes. One exception is the nickel catalyst from the hydrogenation of edible oils which is potentially detrimental to anaerobic digestion systems. However, presently this problem does not generally exist, and nickel levels in wastewaters are infinitesimal to nonexistent. High suspended solids and the oil and grease content of some wastewaters may require that pretreatment be employed for removal of the floatable grease fraction prior to effective biological treatment. Because of the sometimes cyclic nature of waste production in this industry, flow equalization is often required to dampen shock loadings.

These establishments are covered by the following Standard Industrial Classifications (SIC):

2017, 2034, 2038, 2047, 2050, 2052, 2065, 2066, 2067, 2074,
2075, 2076, 2079, 2082, 2083, 2084, 2085, 5182, 2086, 2087,
2095, 2097, 2098, 2099, 5144, 5182

2. Industrial Categorization

A useful categorization for the purpose of raw waste characterization and the establishment of pretreatment information is the following:

a. Vegetable Oil Processing and Refining
b. Beverages, Alcoholic and Non-alcoholic
c. Bakery and Confectionary Products
d. Pet Foods
e. Miscellaneous and Specialty Products (listed in industry description)

3. Process Description

Vegetable Oil Processing and Refining

Vegetable oils are produced from soya beans, cotton, flax, peanuts, olives, sunflower and safflower seeds. The seed is crushed, the oil extracted and refined, and sold for use as shortening, salad and cooking oils, mayonnaise and margarine. Oil is generally extracted from the seed by screwpress expression, hydraulic press or by extraction with some type of solvent (usually hexane). The refining operation involves a complex series of processes intended to remove contaminants, bleach out colors, filter out taste and odors, and to impart to the neutral oils the desired qualities of plasticity, texture, etc. Unit processes include storage and handling caustic refining, bleaching, deodorization, acidulation, winterization, hydrogenation, and plasticizing for margarine.

The major sources of wastewater are acidulation of foots from caustic refining, deodorization, storage and handling, and tank car cleaning. The spent flakes are dried and reprocessed as oil seed meal for eventual sale as animal feed and protein supplement.

Beverages

Malt Brewing

The malt brewing industry produces beer, ale, and malt liquors by fermentation of sugars converted from the starch of various grains i.e. barley,rice,wheat and corn. Grain starch is converted to malt sugar and then to alcohol by mashing, brewing and fermenting. The product is aged, filtered, packaged and marketed. Ground grains are mixed with a ground malt slurry in a mash cooker and lightly boiled. The mixture is filtered. The spent grain waste is sold as feed and the "extract" goes to brewing. Wastewaters include liquor from the spent grain, rinse and clean-up waters.

In the brew kettle the extract is boiled and mixed with hops to produce a liquor called "wort." This hot extract is filtered and sent to fermentation. The spent hops, and "trub" (the insoluble settlings from the hot wort), are added to the spent grains. Spent filter media is hauled away for landfill.

Yeast is added to cooled wort in fermentation tanks where malt sugars are converted to alcohol and carbon dioxide. After aging,the beer is filtered for clarity. The beverage is packed in cans, bottles, and barrels. Lost beer and alkaline washwater are the principal wastes.

Wastewaters are generated from washups. The spent grain from the mashing step may be (1) sold wet (2) screened, pressed as dry as possible, and fire-dried, with the spent grain liquor sewered or (3) screened, pressed and fire-dired with the spent grain liquor concentrated (20-30% solids) in a multi-effect evaporator. The wastes from the grain mashing operating are often the major portion of the plant's waste load.

Malt Manufacture

In this industry barley is converted to malt which is the primary enzyme - producer for starch conversion. The process steps required after cleaning and grading of the grain are:

Steeping - soaking grain in water imparts moisture to grain and washes out colors and tannins. The wash water changes are a major waste.

Germinating - Storing steeped barley in warm, moist atmosphere creates enzymes in grain. Water drained from storage compartments is a source of significant waste.

Kilning - Drying malt to specific moisture content. No wastewaters are generated in this process.

Wines, Brandy and Brandy Spirits

Wines are produced in two general classes: (1) table wines (unfortified) which include the still and sparkling varieties (2) dessert wines and spirits, which are fortified with wine spirits. The wine making process is seasonal, beginning in September and October with gathering, de-stemming and crushing of grapes. The juice, skins and seeds, known as MUST, are fermented for 6 to 8 weeks with an initiating yeast and then screened after color and tannins are sufficiently developed. Clarification and filtration constitute the finishing operations. The residual solids are used as vineyard mulch or poultry feed. Bottling, labeling and casing are the final operations and they produce little waste except for breakage.

Wastewaters from this portion of the industry are principally from equipment washdowns and occasional spills.

Wineries that distill wines to produce wine spirits or brandy have as their major waste, "stillage", the bottoms from the alcohol stills. Stillage can be concentrated in multi-effect evaporators and the residue hauled away or disposed of in evaporation ponds.

Grain Spirits

Distilled, Rectified and Blended Liquors

Various grains and barley malt (enzymes) are mashed, fermented, distilled, aged, and rectified to produce whiskey, vodka, gin, and rum. Cordials and liqueurs are produced by blending. The processes are similar to those of malt beverage production with the addition of distillation and rectification.

Over 80% of the distillery waste is the result of the recovery of spent stillage. Some distilleries dispose of the stillage as is, but most recover it by concentration and drying for cattle feed. Evaporator condensate is a significant source of wastewater.

Molasses distilleries ferment molasses to produce rum. Either cane or citrus molasses is fermented with phosphorous and ammonia nutrients, and yeast to produce a mash. The mash is separated by distillation into rum, amyl oils, and chemical by-products including aldehydes and esters. The chemicals are burned as fuel, the oils are sold, and stillage handling has been previously discussed.

Bottled and Canned Soft Drinks

This industry combines concentrated flavorings, color, sweetener, carbonation and water, and packages the final product. Wastewaters are generated from equipment clean up, spills and bottle washing.

Roasted and Soluble Coffee Processing

Coffee beans are air cleaned, blended, roasted, and marketed as either a ground bean or soluble powder product. Beans may be decaffeinated before roasting by either an organic solvent or a hot water extraction process. They are then rinsed, dewatered, dried and prepared for roasting.

Wastewaters are generated in washing decaffeinated beans, in flushing of the extract centrifuge and in the solvent and caffeine separation process.

Soluble coffee production begins with the passing of hot water through a series of column extractors to extract the soluble materials from freshly roasted and ground coffee beans. The resulting 20-30% solids extract is cooled and then clarified by centrifugation or filtering; later it is usually concentrated to 40% by evaporation or by freeze concentration for more efficient spray or freeze drying. Spent grounds and the residual water associated with the grounds are significant wastes. The grounds are dewatered and landfilled or they are dried for use as boiler fuel; the wastewater that is pressed out of spent grounds is discharged with the cleanings from centrifuges or filters. Other waste sources are the general washdown of the extractors, sludge from the centrifuges or filters, the scaling tank, the heat exchanger and the holding tank. The drying operations produce only cleaning wastewaters.

Coffee

Spent grounds are often dewatered, and the grounds are used as boiler fuel, or landfill. The residual water from spent grounds pressing is a significant wastewater source. Color is also a potential problem from coffee and tea wastes, and activated carbon has shown some potential in the treatment of organic color problems.

Bakery and Confectionary

Conventional bread baking involves a number of dry operations: sifting, mixing, cutting, shaping and baking. This batch system is amenable to dry cleaning techniques and generates little wastewater. On the other hand, newer continuous methods generate considerable amounts of wastewater. In this process, the ingredients are slurried, pumped, extruded and baked. Since the mixture is liquid in much of the process, the equipment must be wet cleaned daily and wastewaters are produced.

Cake production involves high waste generating operations including icing, filling and dusting. Frequent equipment washups are required.

In the production of confectionary products the ingredients are usually mixed, cooked, cooled and aerated. Wastewaters generally are limited to equipment washups.

Pet Foods Industry

Canned, dry, semi-moist pet foods are produced from meat and meat by-products, fish and fish by-products, grains and other additives. The raw materials are blended, cooked and packaged. Dry pet food is prepared by subjecting the materials to an extrusion/expansion process. Daily cleanups and general housekeeping generate wastewaters that contain high BOD and suspended solids. A substantial waste load is generated in the packing and canning of meat based pet foods, since the cans are overfilled prior to sealing.

Miscellaneous and Specialty Products

A large number of items are contained under this heading. Most of them are of a diverse nature and have little relationship to each other with respect to processing, waste characteristics etc. Products included in this group with a significant wasteload are eggs and egg breaking, yeast, hydrolyzate, frozen specialty products, instant tea, bouillon and dehydrated soups, pectin, vinegar, etc. Others having dry processes or insignificant discharges include baking powder, spices, chicory, bread crumbs, non-dairy coffee creamer, peanut butter, manufactured ice, sandwiches, spices, popcorn, desserts, etc.

Pectin, hydrolyzates, instant tea, and yeast generate extremely high waste loads and high volumes. An essential in-plant control for hydrolyzates, yeasts, oil seed extraction, instant coffee, instant tea, egg breaking, etc. is in the separation and alternate disposal of filter cake wastes, condensate underdrains, egg shells, and spent tea leaves. Filters,centrifuges, floatable oil recovery systems, and equalization should be considered as viable in-plant control for most of the miscellaneous and specialty products.

Pectin production, however, generates a high BOD waste. Pectin is a water soluble substance contained in the peel of citrus fruit and used in the preparation of fruit jellies and pharmaceuticals. It is recovered by one of two complex processes, both significant wastewater sources.

4. Wastewater Characterization

Table 8-30-1 contains wastewater characteristics for this industrial group.

5. Control and Treatment Technology

In-Plant Control

Water conservation practices, i.e. high pressure sprays, water meters and segregation of waste streams to enable water reuse can minimize wastewater production. Good housekeeping practices that reduce spills and leaks can reduce washups. The substitution of dry cleanups for water cleanups can significantly reduce the waste load.

Spent grain liquor can be eliminated by direct drying of the grain solids and evaporation of lost beer.

Waste reduction in the manufacture of malt depends upon good control of steep water and maintaining a close spray and refrigeration cycle so that only makeup is needed.

Some wineries have reduced waste volumes by the reuse of cleaning water and by omitting live steam which reduces stillage 15%.

Grain and molasses distillers have reduced wastes by replacing barometric condensers with surface type or mash cookers, coolers and evaporators. Stillage volume can be reduced by substituting indirect heating for live steam injection.

Treatment Technology

Wastes from these industries are generally treated by conventional biological and physical-chemical methods. Because discharges may be intermittent, equalization is often required. Some wastes may be pretreated before discharge to the municipal sewer in order to lighten the organic biodegradable load.

Treatment methods used by the industry include the following:

Pollutant	Treatment Method
BOD	Biological Treatment
	Spray Irrigation/land application
	Flocculation with lime
	Activated carbon
Suspended Solids	Filtration and settling
	Centrifugation
Oil and Grease	Dissolved Air Floatation
	Grease traps
	Sump decanters
	API separators
	Gravity separators
Color	Activated carbon
	Lime precipitation
	Filtration
Nickel	Filtration

TABLE 8-30-1
MISCELLANEOUS FOODS AND BEVERAGES RAW WASTEWATER CHARACTERISTICS (MG/L)

Subcategories	Flow(GPD)	BOD	COD	SS	Oil/Grease
Oil Seed Crushing (except olive oil)		340	815	210	380*
Olive Oil Extraction		30M*-60M*		15M-57M	3M*-20M*
Oil Refining		2M*-7M*	3M*-20M*	1M-3M	500*-4M*
Malt Beverages	700M-8MM	1.4M-2M*		500-700	
Wineries	70M-100M	1.2M*-5.8M*		400-5.7M	
Grain Distillers	25M-600M	200-950*		200-650	
Molasses Distillers	215	35M*		6.7M	
Soft Drink	125	600-2400*		50-100	
Coffee & Tea	70M-180M	350-2400*		700-1500	
Bread & Confectionary	20M-240M	400-1300*		100-400	30-170
Cake	40M-120M	2M*-28M*		1M-5M	500-685
Pet Food	20M-180M	200-12M*		200-9M	
Miscellaneous	200-700M	1M*-6M*		130-1.9M	

Notes: M - thousand
MM - million
* See Appendix 5 for parameters which may be inhibitory to biological systems.

1. General Industry Description

The miscellaneous chemicals industry encompasses a wide range of chemical products, utilizing many different raw materials and unit operations and generating wastewaters with varied characteristics. In general, wastewaters contain BOD, COD, TSS, and metals. This industry includes Standard Industrial Classifications(SIC) 2831, 2833, 2834, 2861, 2879, 2891, 2892, 2895, 2899, 7221, 7333, 7395, 7891, 8062, 8063, 8069.

2. Industrial Categorization

This industry has been divided into the following subcategories:

Major Category	Subcategory
Pharmaceuticals	Fermentative products
	Biological and Natural Extraction products
	Chemical Synthesis/Production
	Mixing/Compounding or Formulation Research
Gum and Wood Chemicals	Char and Charcoal Briquets
	Gum Rosin and Turpentine
	Wood Rosin, Turpentine and Pine Oil
	Tall Oil Rosin, Pitch and Fatty Acids
	Essential Oils
	Rosin Derivatives
Pesticides and Agricultural Chemicals	Halogenated Organic Pesticides
	Organo-Phosphorus Pesticides
	Organo-Nitrogen Pesticides
	Metallo-Organic Pesticides
	Formulators and Packers
Adhesive and Sealants	Animal Glue and Gelatin
	Water-Based Adhesives
	Solvent-Base Adhesives
	Hot Melt Thermoplastic Adhesives
	Dry Blend Adhesives

Major Category	Subcategory
Explosives	Manufacture of Explosives
	Manufacture of Propellants
	Load and Pack Plants
	Specialty Plants
Carbon Black	Furnace Black
	Thermal Black
Photographic Processing	Photographic Processing
Hospitals	Hospitals

3. Process Description

Pharmaceutical Industry

Figure 8-31-1 contains flow diagrams for the production of pharmaceuticals by processes of fermentation, formulation and biological culture.

Fermentation Processes

Fermentation is an important production process in the Pharmaceutical Industry. This is the basic method used for producing most antibiotics (penicillin, streptomycin, etc.) and many of the steroids (cortisone, etc.). The product is produced in batch fermentation tanks in the presence of a particular fungus or bacterium. The culture may be the product, or it may be filtered from the medium and marketed in cake or liquid form as animal feed supplement. The product is extracted from the culture medium through the use of solvents, activated carbon, etc. The antibody is then washed to remove residual impurities, concentrated, filtered and packaged.

The most troublesome waste of the fermentation process, and the one most likely to be involved in water pollution problems, is spent beer. This is the fermented broth from which the valuable fraction, antibiotic or steroid, has been extracted. Spent beer contains a large amount of organic material, protein, and other nutrients. Although spent beer frequently contains high amounts of nitrogen, phosphate, and other plant growth factors, it is also likely to contain salts, like sodium chloride and sodium sulfate, from the extraction processes.

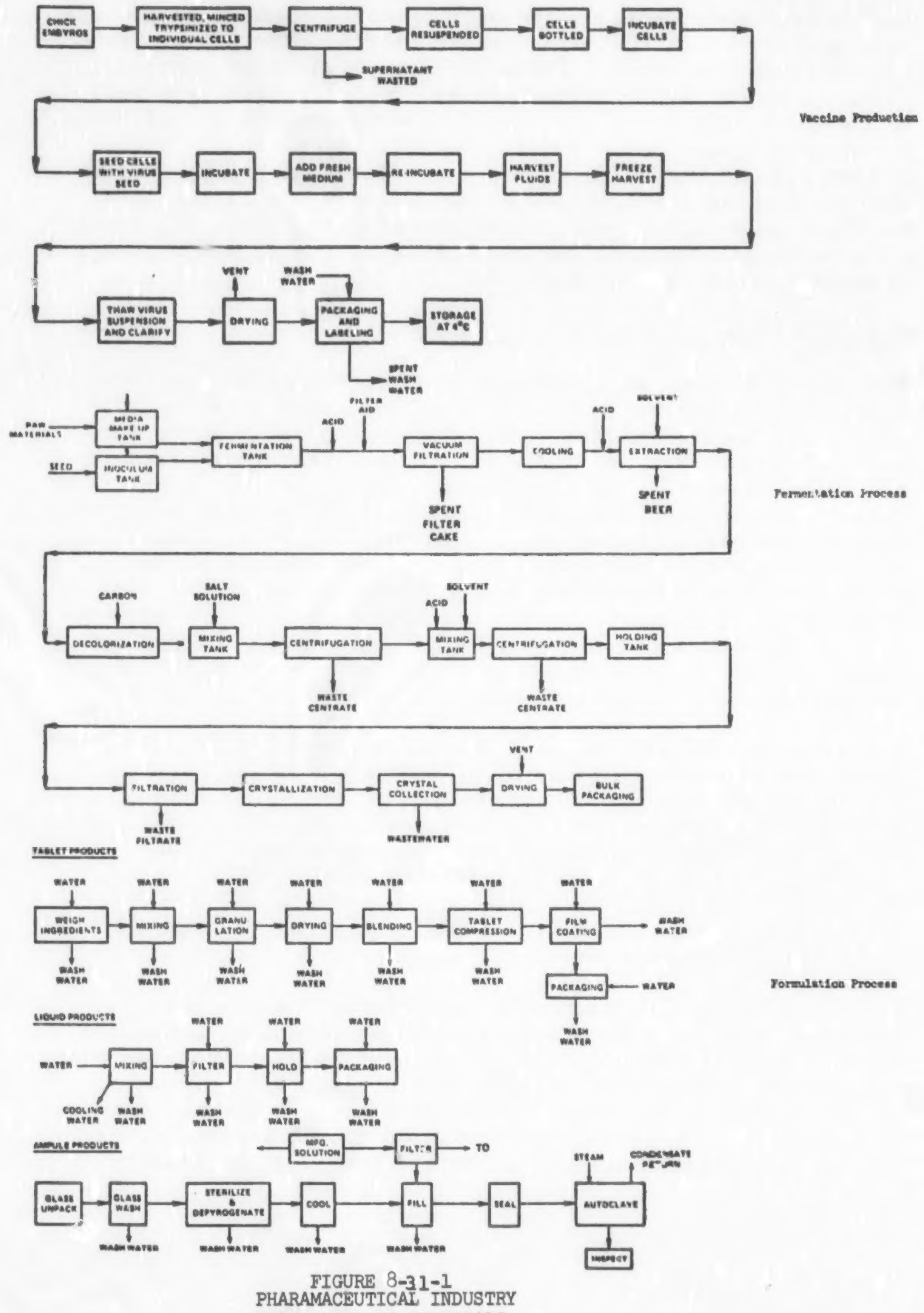

CHICK EMBYROS
HARVESTED, MINCED TRYPSINIZED TO INDIVIDUAL CELLS
CENTRIFUGE
SUPERNATANT WASTED
CELLS RESUSPENDED
CELLS BOTTLED
INCUBATE CELLS
Vaccine Production
SEED CELLS WITH VIRUS SEED
INCUBATE
ADD FRESH MEDIUM
RE-INCUBATE
HARVEST FLUIDS
FREEZE HARVEST
THAW VIRUS SUSPENSION AND CLARIFY
VENT
DRYING
WASH WATER
PACKAGING AND LABELING
SPENT WASH WATER
STORAGE AT 4°C
RAW MATERIALS
MEDIA MAKE UP TANK
SEED
INOCULUM TANK
FERMENTATION TANK
ACID
FILTER AID
VACUUM FILTRATION
SPENT FILTER CAKE
COOLING
ACID
SOLVENT
EXTRACTION
SPENT BEER
Fermentation Process
CARBON
DECOLORIZATION
SALT SOLUTION
MIXING TANK
CENTRIFUGATION
WASTE CENTRATE
ACID
SOLVENT
MIXING TANK
CENTRIFUGATION
WASTE CENTRATE
HOLDING TANK
FILTRATION
WASTE FILTRATE
CRYSTALLIZATION
CRYSTAL COLLECTION
WASTEWATER
VENT
DRYING
BULK PACKAGING
TABLET PRODUCTS
WATER
WEIGH INGREDIENTS
WASH WATER
WATER
MIXING
WASH WATER
WATER
GRANULATION
WASH WATER
WATER
DRYING
WASH WATER
WATER
BLENDING
WASH WATER
WATER
TABLET COMPRESSION
WASH WATER
WATER
FILM COATING
WASH WATER
PACKAGING
WATER
WASH WATER
Formulation Process
LIQUID PRODUCTS
WATER
MIXING
COOLING WATER
WASH WATER
WATER
FILTER
WASH WATER
WATER
HOLD
WASH WATER
WATER
PACKAGING
WASH WATER
AMPULE PRODUCTS
MFG. SOLUTION
FILTER
TO
GLASS UNPACK
GLASS WASH
WASH WATER
STERILIZE & DEPYROGENATE
WASH WATER
COOL
WASH WATER
FILL
WASH WATER
SEAL
STEAM
CONDENSATE RETURN
AUTOCLAVE
INSPECT

FIGURE 8-31-1
PHARAMACEUTICAL INDUSTRY
MISCELLANEOUS CHEMICALS

This subcategory includes the unit operations which follow the fermentation steps that are used to retrieve the product from the fermentation broth. These include physical separation steps, such as vacuum filtration and centrifugation, as well as chemical separation via solvent extraction and distillation. Fermentation requires extensive quantities of water. The primary liquid wastes include the fermentation beers; inorganic solids, such as diatomaceous earth, which are utilized as a pre-coat or an aid to the filtration process; floor and equipment washings; chemical wastes such as solvents; and barometric condenser water from evaporation.

Biological and Natural Extraction Process

Biological Product Manufacturers produce bacterial and virus vaccines, toxoids and analogous products (such as allergenic extracts), serums, plasmas, and other blood derivatives for human or veterinary use. The primary manufacturing steps in blood fractionation include chemical precipitation, clarification, extraction, and centrifugation. The primary wastewater sources are precipitates, supernatants, centrates, waste alcohols, and tank washings. The precipitates and waste alcohols can be incinerated or reclaimed, while dilute wastes (supernatants, centrates, and tank washings) are sewered. The production procedures for vaccines are generally lengthy and involve numerous batch operations. Unit operations include incubation, centrifugation, staining, freezing, drying, etc.

Liquid wastes associated with the process consist primarily of spent media broth, waste eggs, glassware and vessel washings, animal wastes, bad batches of production seed and/or final product, and scrubber water from air pollution control equipment. Spent media broth, bad batches, waste eggs, animal carcasses, and contaminated feces are normally incinerated. Wastes from small non-infected control animals may be landfilled. Equipment washings, animal cage washings, and scrubber blowdowns are usually sewered.

Natural extractions manufacturing includes the processing (grading, grinding, and milling) of bulk botanical drugs and herbs. Establishments primarily engaged in manufacturing agar and similar products of natural origin, endocrine products, manufacturing or isolating basic vitamins, and isolating active medicinal principals such as alkaloids from botanical drugs and herbs are also included in this industry. The primary wastewater sources include floor washings, residues, equipment and vessel wash waters and spills. To the maximum extent possible, bad batches are corrected rather than discarded. When bad batches cannot be corrected, liquids are generally discharged to the plant sewer system. Solid wastes are usually landfilled or incinerated.

Chemical Synthesis

The production of chemical synthesis products is very similar to fine chemicals production, and uses the following major unit processes: reaction, extraction, concentration, separation, solvent recovery, and drying. The synthesis reactions are generally batch types which are followed by extraction of the product. Extraction of the pharmaceutical product is often accomplished through solvents. The product may then be washed, concentrated and filtered to the desired purity and dried. The major wastewater sources include tank washes, equipment washes, spent cooling water, and condenser discharges. These wastes are generally amenable to biological treatment.

Mixing/Compounding or Formulation

Formulation operations for synthesis products may be either dry or wet. Dry production involves dry mixing, tableting or capsuling, capsule manufacturing, and packaging. Process equipment is generally vacuum cleaned to remove dry solids, and then is washed down. Scrubber blowdown from air pollution control devices may also be a wastewater source. The primary wastewater sources include equipment washings and spills.

Research

Research facilities do not produce marketable products but generate wastewaters from equipment washings and animal cage washwaters. A common problem is the disposal of flammable solvents which can result in explosions and fires.

Gum and Wood Chemicals

Char and Charcoal Briquets

Char or charcoal is produced by the carbonization of wood, which is the thermal decomposition of raw wood. During the decomposition of the wood, distillates are formed and leave the kiln with the flue gases. The condensable distillates are called pyroligneous acids which contain methanol, acetic acid, acetone, tars, oil, and water. This distillate may be recovered or burned. No process wastewaters are generated.

Gum Rosin and Turpentine

The crude gum raw material is obtained by gum farmers who collect the gum from pine trees. The gum is filtered to remove impurities and then distilled to separate the turpentine. Wastewaters are produced from crude gum wash, still condensate, and dehydration of brine operations. Wastes contain BOD and COD.

Wood Rosin, Turpentine and Pine Oil

These materials are manufactured from stumps obtained from cut-over pine forests. The stumps are washed and reduced to wood chips and then the products are extracted and steamed from the chips. Washwaters are recycled. Only condensate wastewaters are produced containing BOD and COD. Figure 8-31-2 is a flow diagram for this process.

Tall Oil Rosin, Fatty Acids and Pitch

These products are produced by distillation of crude tall oil, a chemical wood pulp by-product, in an operation similar to oil refinery distillation. Very few process wastes are produced. The major waste flow is from non-contact cooling water.

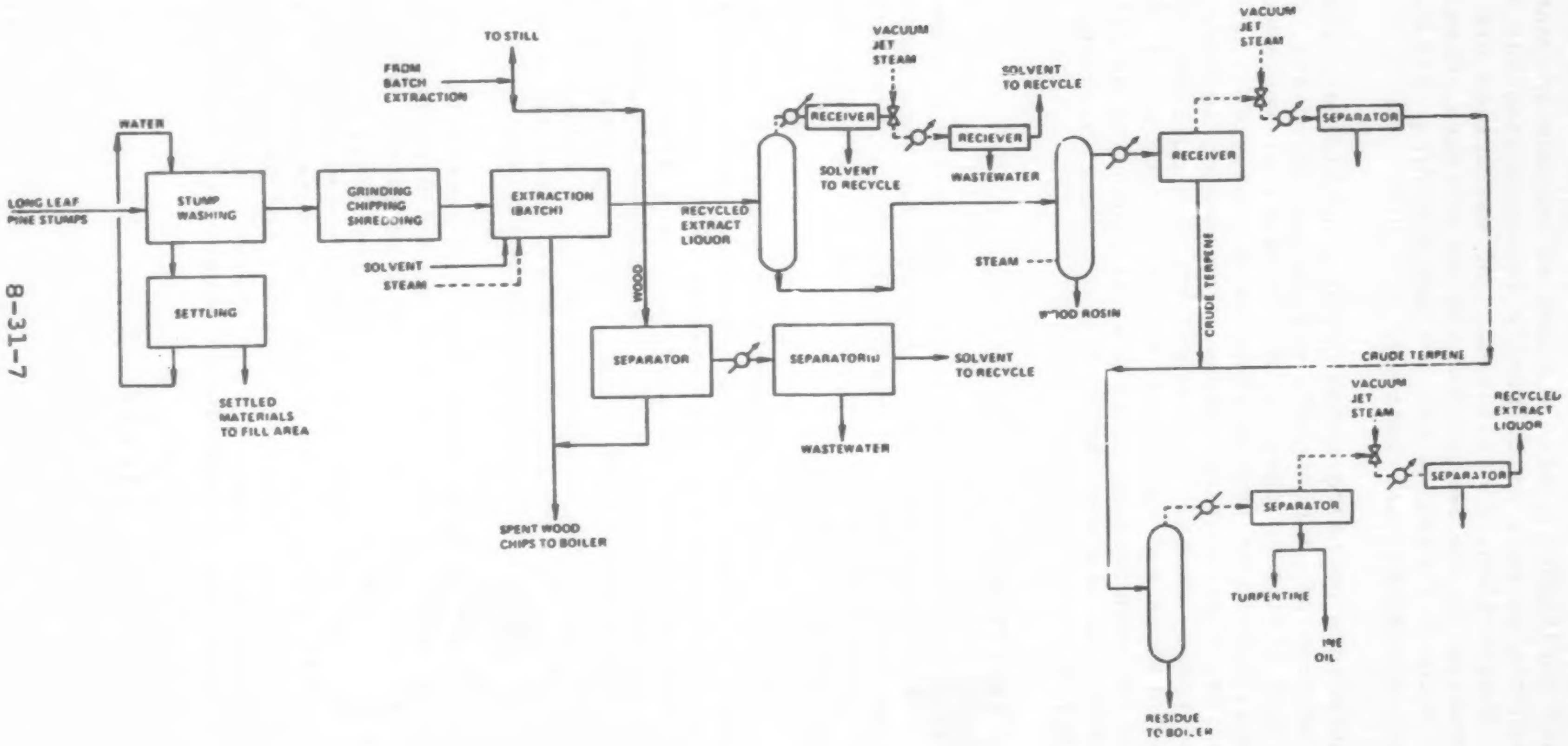
Pesticides and Agricultural Chemicals Industry

Pesticide plants which manufacture active ingredient products use many diverse manufacturing processes. Rarely does a plant employ all of the processes found in the industry, but most plants use several in series. The principal processes utilized include chemical synthesis, separation, recovery, purification and product finishing, such as drying.

Chemical synthesis can include chlorination, alkylation, nitration, and many other substitutive reactions. Separation processes include filtration, decantation, and centrifuging.

Figure 8-31-2

WOOD ROSIN PINE OIL, AND TURPENTINE PRODUCTION VIA SOLVENT EXTRATION


LONG LEAF PINE STUMPS
WATER
STUMP WASHING
SETTLING
SETTLED MATERIALS TO FILL AREA
GRINDING CHIPPING SHREDDING
SOLVENT
STEAM
EXTRACTION (BATCH)
TO STILL
FROM BATCH EXTRACTION
WOOD
SEPARATOR
SPENT WOOD CHIPS TO BOILER
SEPARATOR(s)
SOLVENT TO RECYCLE
WASTEWATER
RECYCLED EXTRACT LIQUOR
RECEIVER
SOLVENT TO RECYCLE
VACUUM JET STEAM
RECIEVER
SOLVENT TO RECYCLE
WASTEWATER
STEAM
WOOD ROSIN
RECEIVER
CRUDE TERPENE
VACUUM JET STEAM
SEPARATOR
CRUDE TERPENE
VACUUM JET STEAM
SEPARATOR
RECYCLED EXTRACT LIQUOR
SEPARATOR
TURPENTINE
PINE OIL
RESIDUE TO BOILER

Recovery and purification are utilized to reclaim solvents or excess reactants as well as to purify intermediates and final products. Evaporation, distillation, and extraction are common processes in the Pesticides and Agricultural Chemicals Industry. Product finishing can include blending, dilution, pelletizing, packaging, and canning.

In the manufacture of halogenated organic pesticides, the principal sources of high organic wastes are decanting, distillation, and stripping operations. Sources of wastewater from the manufacture of organo-phosphorus pesticides include decanter units, distillation towers, overhead collectors, solvent strippers, caustic scrubbers, contact cooling, hydrolyzing, and product and equipment washing. Sources of wastewaters from the manufacture of organo-nitrogen and metallo-organic pesticides are similar to the two other products mentioned above.

Adhesive and Sealants

The manufacturing processes for all subcategories within the industry are basically the same. From one-man garage-type operations to large industrial complexes, the manufacturing process consists of mixing or compounding the various components in batch mix tanks or kettles.

Both water base and organic solvent base adhesives are produced by mixing the raw materials in mixing tanks under ambient temperatures or heating the tank contents with steam. The non-solvent base adhesives (thermoplastic and dry-blend adhesives) are produced in mixing tanks also. Thermoplastic adhesives require heat while dry-blends do not. All production processes described above are batch processes. The one exception is animal glue production, which involves hot water applications for the extraction of glue from the raw materials.

Solvents are needed in most adhesives to disperse the binder to a spreadable liquid form. In most wood-and paper-bonding adhesives the solvent is water. In many adhesives based on synthetic resins, rubbers, and even natural gums, a variety of organic solvents are required to achieve the necessary solubility and to provide some minimum percentage of base solids. However, thermoplastic adhesives and dry blended adhesive materials are composed completely of solids and contain neither water nor solvent-based materials. Polymeric, thermoplastic solids are converted to mobile fluids when subjected to sufficient amounts of heat.

The main source of wastewater is the washing of the process vessels and lines. Most adhesive industries discharge to publicly-owned treatment works. Wastes are high in BOD, COD and TSS.

Explosives

The general production process for the manufacturing of explosives involves the nitration of an organic molecule. Raw materials used in this process are nitric acid, acting as the nitrate source, and sulfuric or acetic acid, acting as a dehydrating agent. Examples of the organic molecules used are glycerin, toluene, resorsinol, hexamine and cellulose. After nitration, these organic molecules produce the following products: nitroglycerin and dinitroglycerin; trinitrotoluene and dinitrotoluene; trinitroresorscinol; nitromanite; and nitrocellulose, respectively. Additional production processes involve the formation of highly sensitive initiators with nitrogen salts as a nitrogen source. An example of this product would be lead azide.

Wastewaters are generally very low in pH and can be high in BOD, COD and nitrates. Wastes can also contain concentrations of the explosives produced.

Figure 8-31-3 is a flow diagram for the nitroglycerin manufacturing process.

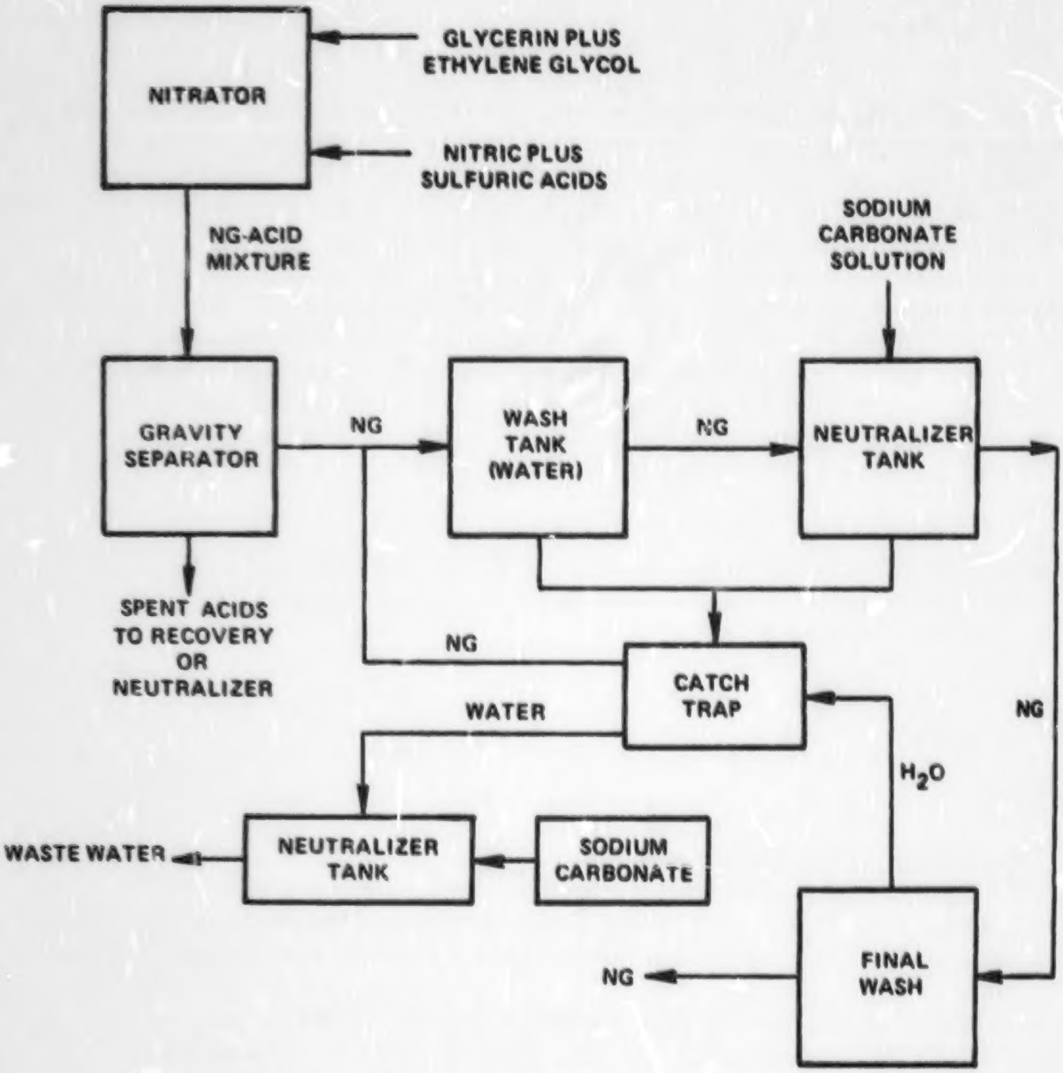
Carbon Black

The manufacturing processes used to manufacture carbon black consist of the furnace, thermal, channel, and lamp black processes. The final product from each of these processes is carbon black, differing only in particle size and structure.

Furnace black is produced by the incomplete combustion of hydrocarbons. The raw materials consumed in the manufacture of carbon black consist of hydrocarbons. Liquid hydrocarbons are used in the furnace process. The most desirable feed stock oil for the furnace process comes from near the bottom of the refinery barrel and is similar in many respects to residual fuel oil. It is low in sulfur and high in aromatics and olefins. This process is a net user of water and generally has no process contact wastewaters.

FIGURE 8-31 -3

TYPICAL NITROGLYCERIN PRODUCTION SCHEMATIC


NITRATOR
GLYCERIN PLUS ETHYLENE GLYCOL
NITRIC PLUS SULFURIC ACIDS
NG-ACID MIXTURE
SODIUM CARBONATE SOLUTION
GRAVITY SEPARATOR
NG
WASH TANK (WATER)
NG
NEUTRALIZER TANK
SPENT ACIDS TO RECOVERY OR NEUTRALIZER
NG
CATCH TRAP
WATER
NG
H_2O
WASTE WATER
NEUTRALIZER TANK
SODIUM CARBONATE
NG
FINAL WASH

Thermal blacks are produced by cracking of natural gas to form carbon and hydrogen gas. The major wastewater source from this process is the blowdown from a recirculating dehumidifier system.

Channel black is produced by impingement of under-ventilated natural gas flames on moving, continuously scraped channels.

Lamp blacks are manufactured by the burning of petroleum or coal tar residues in open shallow pans.

Photographic Processing

Most commercial photoprocessors handle many square feet of film and paper with automatic processing machines. The basic machines are called the "dip and dunk" or "rack and tank" types, which consist of a series of tanks with each tank containing a photoprocessing solution. These solutions impart the desired effect on the film or paper in each progressive step of development. Continuous length processors are used by most large firms, and roller transports are used in graphic arts and for hospital X-ray films.

During photoprocessing, many changes occur within the processing solutions. Because of these changes, the chemicals used in photo-processing need to be replaced, strengthened or replenished. Developing agents become oxidized and exhausted; developer activators and preservatives wear out; anti-foggants become used up; bromides or other halides resulting from the reduction of the silver by the developer become more concentrated; acid short stops become neutralized; and the removal of silver from the emulsion causes increased concentrations of silver in the fixers or hypo baths. Chemicals are added to maintain the correct chemical strength and photographic properties. When a replenisher is added, its volume must be sufficient to cause enough overflow of the unwanted by-products. Overflows from the processing tanks caused by the addition of replenishers and wash water overflows are the two sources of effluent from photoprocessing.

Process wastewaters include both photoprocessing solution overflows and washwaters; together, these spent waters are high in BOD, COD, TOC, TDS, silver and cyanide. Generally, the pollutants of significance are the same for both color and black and white photofinishing operations with the exception of ferrocyanide which is generated during the bleaching step in color development.

Hospitals

The three major areas in a hospital which generate wastewaters are patient rooms, laundries, and cafeterias. Sanitary flows are the primary wastes from hospital patient rooms and, obviously, the more beds a hospital has, the more significant this flow will be. Cafeterias are another large contributer to the wastewaters generated by hospitals. The cleaning of foodstuffs, preparation of meals, washing of dishes, and floor and equipment cleaning are all activities which generate wastewaters from a cafeteria. These wastes usually contain organic matter, in dissolved and colloidal state, and oils and greases in varying degrees of concentration. The third major contributor of wastewaters in a hospital is laundries. Laundry wastes originate from the use of soap, soda, and detergents in removing grease, dirt, blood, and starch from soiled clothing and linen. Laundry wastes generally have a high turbidity, alkalinity, and BOD content.

Three other areas in a hospital which discharge smaller quantities of wastewaters are surgical rooms, laboratories, and X-ray departments. Surgical room wastewaters are primarily washwaters from cleaning activities. Laboratory wastes generally consist of solvents, glassware washwater, and various reagents used in the laboratory. Research hospitals may also have animal cage washings in their laboratory wastes. X-ray departments are an additional source of wastewaters. These wastes consist of spent solutions of developer and fixer, containing thiosulfates and compounds of silver. The solutions are usually alkaline and contain various organic reducing agents. Most hospitals recover the silver from spent X-ray film developing solutions. All pathological wastes from surgical suites are collected and disposed of in hospital pathological incinerators.

Some hospitals generate radioactive wastes from diagnostic and therapeutic uses. Iodine-131 and phosphorus-32 are the radioisotopes which predominate in hospital radioactive wastes.

Fortunately, these possess short half-lives, and simple detention tanks can render them inactive. The handling of radioactive waste is closely monitored by AEC, and these wastes are not discharged to the hospital sewer system.

4. Wastewater Characterization

Tables 8-31-1 through 8-31-6 provide waste characterization data for the industries covered in this description.

5. Control and Treatment Technology

In-Plant Control

Pharmaceutical Industry - Good housekeeping consists of the use of dry cleaning techniques (vacuum cleaning) in place of wet systems, separate containment of toxic substances, and containment of spills and storm water.

Other in-plant controls consist of the following:

1) The replacement of water sprays with exchangers in barometric condensers.
2) Recycling of water used in water sealed pumps.
3) Recovery of waste solvents, and other chemicals.
4) Reuse of wastewaters (e.g. cooling water).

Gum and Wood Chemicals - Specific in-plant control measures have not been identified for this industry.

Pesticides and Agricultural Chemicals - Waste segregation is an important in-plant control measure, since high organic loading streams will require different treatment schemes than low organic loading streams. The use of dry cleanup systems can also reduce wastewater flows. Steam jet ejectors and barometric condensers can be replaced in most cases with vacuum pumps and surface condenser systems.

Adhesive and Sealants - Some in-plant controls that are applicable to this industry are:

1) Rinse recycle to reduce rinse water volumes.
2) Recovery of by-products that can be sold instead of discharged as a waste stream.

TABLE 8-31-1
PHARMACEUTICAL INDUSTRY
RAW WASTEWATER CHARACTERIZATION

PARAMETERS (mg/l)	SUBCATEGORY				
	Fermentative Products	Biological and Natural Extraction Products	Chemical Synthesis	Mixing and Compounding	Research
Flow, GPD	80M - 500M	20M - 200M	30M - 1.5MM	10M - 400M	20M - 300M
Flow Type	B		B		
BOD	4M*- 11M*	100-600	500 - 5M*	250 - 2M*	100 - 300
TSS	800 - 7M	10 - 50	200 - 900	100 - 500	200 - 500
TDS	High		Avg - High		
COD	9M* - 15M*	400 - 1M*	3M* - 10M*	500 - 4M*	200 - 600
TOC	1.8M - 10M	30 - 200	900 - 3M	200 - 900	50 - 150
Cyanide			Present		
pH	4* - 8	6* - 8	1*-11*	6*- 8	6*- 8
Color	Avg - High		Avg - High		
Detergents	Present		Present		
Metals			Present		

Notes:

M = 1,000
MM = 1,000,000
B - Batch Process
* See Appendix 5 for parameters which may be inhibitory to biological systems

TABLE 8-31-2
GUM AND WOOD CHEMICALS INDUSTRY
RAW WASTEWATER CHARACTERIZATION

PARAMETERS (mg/l)	SUBCATEGORY Char and Charcoal	Gum Rosin and Turpentine	Wood Rosin, Turpentine & Pine Oil	Tall Oil Rosin, Pitch, Fatty Acids	Essential Oils	Rosin Derivatives
BOD	No					
TSS	Process	140	30	0	6	50
TDS	Flow	3600*	700	650	50	7300*
Color		200	100	40	-	-
Nitrogen (Kjeldahl)		30	5	0	10	13
Oil and Grease		400*	50*	300*	0.5	360*
Zinc		15*				7*
Phenol				20		60

Notes: * See Appendix 5 for parameters which may be inhibitory to biological systems.

TABLE 8-31-3
PESTICIDES AND AGRICULTURAL CHEMICALS RAW WASTEWATER CHARACTERISTICS

PARAMETERS (mg/1)	SUBCATEGORY				
	Halogenated Organic Pesticides	Organic Phosphorus Pesticides	Organic Nitrogen Pesticides	Metallo-Organic Pesticides	Formulators and Packers
BOD	125 - 8.5M*	140 - 750*	1.2M* - 2.5M*	20 - 800*	150 - 1.6M*
TSS	100 - 250	10 - 100	10 - 2M	1.5M - 3M	100 - 650
COD	850 - 16M*	350 - 1.8M*	800 - 15M*	1.5M*- 2.2M*	500 - 6M*
TOC	650 - 8.4M	100 - 4M	450 - 5.3M	80	-
TDS			2M* - 44M*		

Notes: M = 1,000

MM = 1,000,000

* See Appendix 5 for parameters which may be inhibitory to biological systems.

TABLE 8-31-4
ADHESIVE AND SEALANTS
RAW WASTEWATER CHARACTERISTICS

PARAMETERS (mg/l)	SUBCATEGORY					
	Animal Glue and Gelatin	Water Based Adhesives	Solvent Based Adhesives w/Contaminated Water	Solvent Based Adhesives w/o Contaminated Water	Hot Melt Thermo-Plastic Adhesives	Dry Blend Adhesives
Flow, GPD	3MM	3M-10M	6M	70M-350M	No Waste Flow	No Waste Flow
BOD	1.2M*-4.8M*	2.1M*-4.2M*	13M*	No Contaminated Waste Water		
TSS	1.7M -4.5M	2.1M -4.3M	36			
COD	10M*	16M*	22M*			
TOC	2.6M	3.8M -7.7M	4.2M			
pH	9-12*	9				
Nitrogen-NH_3	16	5-20	20			
Chromium	10*-20*					
Oil and Grease	400*-1.5M *					

Notes:

M = 1,000

MM= 1,000,000

* See Appendix 5 for parameters which may be inhibitory to biological systems

TABLE 8-31-5
EXPLOSIVES INDUSTRY
RAW WASTEWATER CHARACTERISTICS

PARAMETERS (mg/1)	SUBCATEGORY			
	Manufacture of Explosives	Manufacture of Propellants	Load and Pack Plants	Specialty Plants
BOD	20 - 1M*	200	1M*	1M* - 12M*
TSS	10 - 1.3M	100 - 1M	1 - 700	1 - 60M
COD	60 - 3.4M*	200 - 1.2M*	8 - 8.5M*	11M*- 50M*
TOC	12 - 1.5M	30 - 130	5 - 550	5.7M
pH	Variable	Variable	Variable	Variable
Nitrogen (nitrate)	25 - 7M*	1 - 4M*	.4 - 12	.5 - 5M*
Explosives	Present	Present	Present	Present

Notes:

M = 1,000

MM = 1,000,000

* See Appendix 5 for parameters which may be inhibitory to biological systems

TABLE 8-31-6
CARBON BLACK, PHOTOGRAPHIC, AND HOSPITAL INDUSTRIES RAW WASTEWATER CHARACTERISTICS

PARAMETERS (mg/l)	S U B C A T E G O R Y		
	Carbon Black Industry	Photographic Industry	Hospitals
BOD	No	300	100-400
TSS	Data	25	60-200
TDS		2,000*	
COD		1,000	300-800
TOC		300	100-300
Cyanide		6*	
Nitrogen (Kjeldahl)		100	
Iron		20*	
Silver		0.5	
Boron		18*	

Notes:

M = 1,000

MM = 1,000,000

* See Appendix 5 for parameters which may be inhibitory to biological systems

3) Minimize equipment washouts.
4) The use of steam instead of water reduces the wastewater volume.

Explosives Industry - Many products are manufactured by a dry process, so that the only waste streams come from cleanup of spills and leaks. Dry cleanup systems should therefore be used.

In many plants, water is used to transport the material throughout the facility, and to purify the product. This water need not be of high quality, and recycle can reduce the waste produced from this operation. Separation of contact and non-contact waters can reduce the size of treatment systems, and the volume of flow discharged.

Carbon Black Industry - Due to the competitive nature of this industry, product and water recycle is generally practiced. The major item for which reduction of wastewater has been accomplished has been the use of bag filters for carbon black recovery instead of wet scrubbers.

Photographic Processing - The major in-plant control practiced by this industry is metal recovery. Silver can be recovered by metallic replacement, electrolytic plating, and chemical precipitation. The use of squeegees for inhibiting carry-over from one process tank to another reduces the waste load from the plants. Depleted treatment baths should be discharged gradually into the sewer in order to minimize treatment plant upsets.

Hospitals - The most common in-plant controls practiced by hospitals are the elimination of mercury discharges and the recovery of silver from spent X-ray developer.

Treatment Technology

The following industries use biological treatment systems:

1) Pharmaceutical Industry
2) Gum and Wood
3) Pesticides
4) Explosives (only in a small number of plants)
5) Photographic processing
6) Hospitals (only a few hospitals treat their own wastes).

Since adhesive and sealant plants mostly discharge to POTW's, and their wastes are generally weak, only clarification in lagoons is practiced for BOD removal.

The effluents from thermal black plants in the carbon black industry are sent to evaporation ponds, thus generating no discharge.

Table 8-31-7 provides removal efficiencies for biological treatment systems used in the above-mentioned industries.

TABLE 8-31-7
MISCELLANEOUS CHEMICALS INDUSTRY WASTEWATER TREATMENT PRACTICES

Pollutant and Method	Industry, Removal Efficiency, Percent					
	Pharmaceuticals	Gum and Wood	Pesticides	Explosives	Photographic Processing	Hospital
BOD						
Biological Treatment	70-99	95	No Data	93	30-90	90
COD						
Biological Treatment	40-96	73	No Data	72	No Data	No Data
TSS						
Biological Treatment	75-95	50	No Data	88	No Data	80-90

1. General Industry Description

Laundry facilities use a variety of methods to obtain a clean product. With the exception of dry cleaning plants, the industry uses substantial quantities of process waters. Presently more than 90% of all laundries discharge to municipal sewer systems and may account for 5-10% of the average daily flow of sewage. It is also a significant flow from a quality standpoint,contributing from 10-20 times as much contamination as the average domestic waste. It is usually strongly alkaline, highly colored, and contains large quantities of soap or synthetic detergents, soda ash, grease, dirt and dyes. The BOD is 2-5 times that of domestic sewage.

This industry includes Standard Industrial Classifications (SIC) 7211, 7213, 7214, 7215, 7216, 7217, 7218, 7219 and 7542.

2. Industrial Categorization

This industry has been divided into the following subcategories:

Subcategory 1 - Industrial Laundries

Subcategory 2 - Linen Supply
Power Laundries, Family and Commercial
Diaper Service

Subcategory 3 - Auto Wash Establishments

Subcategory 4 - Carpet and Upholstery Cleaning

Subcategory 5 - Coin operated Laundries and Dry Cleaning
Laundry and Garment Service Not Elswhere Classified

Subcategory 6 - Dry Cleaning Plants, Except Rug Cleaning

3. Process Description

Industrial Laundries

Industrial laundries are located in highly populated areas, and discharge large quantities of high strength wastewater into municipal treatment facilities. A medium sized industrial laundry processes between 80,000 - 100,000 pounds of dry wash per week. Articles are subjected to a series of wash and rinse operations to remove oil and grease, and to loosen soil. Some items are dyed and rinsed. Excess water is extracted and the items are dried in a dryer. The wastewater has the appearance of thin oily mud and contains material from towels used by printers, tool and die makers, filling station attendants, etc. The soil may be in the form of paints, varnishes, lacquer, latex rubber, ketone solvents, inks and dyes. Thus laundry effluent contains products its customers are using plus laundry agents including alkalies, soaps, detergents, bleaches, starches, blueing compounds, fabric softeners, fungicides, petroleum solvents and enzymes.

Linen Supply, Power Laundries (Family and Commercial) and Diaper Services

This subcategory has the second strongest average waste load. Operations are similar to industrial laundries, except that two sudsing stages are used, with a rinse step between them. In addition, a sour step is utilized in place of the dye step mentioned above. A sour is an acid chemical added at the end of the operation to negate the swelling effect of the alkali. Starch as well as other compounds are added frequently to linen wash loads. The waste characteristics from this subcategory are similar to industrial laundries, except that the strength of the waste is usually lower.

Auto Wash Establishments

Tunnel Type - The vehicle is pulled through a "Tunnel" type area past different operating stations. The operation is generally fully automatic, with operations such as interior cleaning, wiping, and drying performed manually.

Bay Type - In this coin operated type of auto wash,the customer parks his car in a bay area, and a wand type of water spray unit is used to soap up and rinse down the vehicle.

Wastes from both type of auto wash systems contain high amounts of total solids, suspended solids, oil, grease and BOD.

Carpet and Upholstery Cleaning

At present, about 30% of all rug cleaning operations are done in the home.

In a typical in-plant cleaning operation, the rug is first beaten to remove dust and dry solids and is then wetted with water and a mild, dilute detergent. The rug then passes through a system of either rollers or brushes which work the detergent into the fiber. A clean water rinse follows, the excess water is squeezed out and the rug is air dried.

Upholstery Cleaning is basically a dry process, and therefore, no wastewater is produced.

Coin Operated Laundries, Dry Cleaning Facilities and Laundry and Garment Services not Elsewhere Classified

Most coin-operated laundries contain between 25 and 35 machines, each of which uses 25-30 gallons of water per washing cycle. An average weekly wastewater volume of 50,000 gallons can be expected from such an operation. Approximately 100 pounds of commercial detergent would be used per week. Fifteen cycles per day is about standard for a washer, but many laundromats use machines that do 25 cycles or more per day.

Coin-operated dry cleaning is a solvent cleaning process with no process wastewater discharge.

Laundry and garment services not elsewhere classified include Chinese and French hand laundries, facilities where clothes are altered and repaired, and pillow-cleaning operations. Since their effluent is small in both volume and contaminant levels, this operation has not been included in this summary.

As a group, the effluent of industries in this subcategory is weaker than domestic sewage and can, therefore, be handled easily by municipal treatment plants.

Dry Cleaning Plants, Except Rug Cleaning

A solvent is used to remove the dirt from the fabric and then the solvent is recovered and recycled by a filter system.

Soil extracted from the cleaned materials should be disposed of by a scavenger. No wastewaters are usually generated.

4. Wastewater Characterization

Table 8-32-1 contains raw wastewater characteristics for this industry.

5. Control and Treatment Technology

In-Plant Control - Industrial laundries can reduce the oil and grease content of wastewater by 80-85% by pretreatment of laundry using dry cleaning methods before washing.

Thirty percent of the auto laundries recycle wash and/or rinse water with varying degrees of treatment. Washwater can be recycled after settling out the solids. Rinse waters have higher

Table 8-32-1
Auto and Other Laundries
Raw Wastewater Characteristics

Waste Parameter (mg/l)	Subcategories						
	1 Industrial Laundries	2 Linen Supply Only	3 Auto Washes Tunnel Type	3 Auto Washes Bay Type	4 Carpet and Upholstery Cleaning	5 Laundromats Only	6 Dry Cleaning Except Rug Cleaning
BOD	650*-1300*	100- 800*	30-80	15- 170	No Data	120-250	No Waste
TSS	650 -5000	500-1500	160-230	95- 850		15-300	
TDS	1500*-6500*	1700*-2000	570-1700*	630-2500*		100-2000*	
COD		2100*-5100*	150-275			65-1400*	
pH	11*-13*	10.3*-11.2*	8.7-9.1			5.1-10*	
Chromium	1-4*	0.06	0-1				
Copper	0.2-9*	0.3	0-0.3				
Lead	3*-36*	0.7*	0-1*				
Zinc	0.5*-9*	0.5*	0.3*-0.4*				
Cadmium	0-0.6*	0.04*	0-0.04*				
Iron	3-125*		3-4				
Nickel	1-2.5*	2	0-0.7				
Mercury	0.001-0.007						
Oil & Grease	400*-3700*	200*-1200*	0-0.3	40-200*			

Note: *See Appendix 5 for parameters which may be inhibitory to biological systems.

purity requirements and can be treated with a germicide and de-emulsifier, then clarified and screened prior to recycling.

Treatment Technology - One process that has shown some promise in the treatment of laundry wastewater is the "Flotation Diatomaceous Earth (DE) Filter System." In this system the wastewater is first treated with calcium chloride at a high pH to break down any emulsions. Air flotation and skimming then removed the bulk of the oil and grease. The flotation effluent is then passed through a diatomaceous earth filter and the scum collected is concentrated by vacuum filtration. Limited data for removal efficiencies are shown in Table 8-32 -2.

Table 8-32-2
Auto and Other Laundries
Wastewater Treatment Practices

Pollutant and Method	Removal Efficiency (Per Cent) Industrial 1	Linen Supply 2	Coin Operated Laundromats 5
BOD			
Flotation Diatomaceous Earth Filter	50-73		73
Oxidation - Activated Carbon		92	
Alum Coagulation - Activated Carbon			87
Suspended Solids			
Flotation Diatomaceous Earth Filter	88		
Oxidation - Activated Carbon	90		
Filtration - Aerobic Digestion		99	
Alum Coagulation - Activated Carbon			92
Oil and Grease			
Flotation Diatomaceous Earth Filter	80-99		
Filtration - Aerobic Digestion		84	
Flotation - Clarification			86

1. General Industry Description

The paint and ink manufacturing industry is essentially a product formulation industry, in that few, if any, of the raw materials are manufactured on site. The major products consist of interior and exterior paints, industrial finishes for such products as automobiles, appliances, furniture; varnish and lacquer; putty; caulking compounds; sealants; paint and varnish removers; and printing inks. The principal raw materials are oils, resins, pigments and solvents.

The majority of plants in this industry discharge to publicly owned treatment works. Wastewaters are high in BOD, COD, suspended solids and may contain metals. Establishments engaged in this industry are included in Standard Industrial Classifications(SIC) 2851 and 2893.

2. Industrial Categorization

Major Category	Subcategory
Paint	Oil Base Paint Water Base Paint
Ink	Oil Base Ink Water Base Ink

3. Process Description

Both paint and ink can be either oil-base or water-base but there is little difference in the production processes used. The major production difference is in the carrying agent--oil-base paints and inks are dispersed in an oil mixture, while water-base paints and inks are dispersed in water with a biodegradable surfactant used as the dispersing agent. Another significant difference is in the cleanup procedures. Since the water-base products contain surfactants, it is much easier to clean up the tubs with water. The tubs used to make the oil base products are generally cleaned with an organic solvent or with a strong caustic solution.

All paints and inks are generally made in batches. The major difference in the size of a plant is in the size of the batches. A small plant will make up batches of from 400 to 1,900 liters (100 to 500 gal.) while a large plant will manufacture batches of up to 23,000 liters (6,000 gal.). There are generally too many color formulations to make a continuous process feasible.

Oil Base Paint and Ink

There are three major steps in the oil-base paint and ink manufacturing process: (1) mixing and grinding of raw materials, (2) tinting and thinning, and (3) filling operations.

At most plants, the mixing and grinding of raw materials for oil-base paints and inks are accomplished in one production step. For high gloss paints, the pigments and a portion of the binder and vehicle are mixed into a paste of a specified consistency. This paste is fed to a grinder, which disperses the pigments by breaking down particle aggregates rather than by reducing the particle size. Two types of grinders are ordinarily used for this purpose: pebble or steel ball mills, or roll-type mills. Other paints are mixed and dispersed in a mixer using a saw-toothed dispersing blade.

In the next stage of production, the material is transferred to tinting and thinning tanks, occasionally by means of portable transfer tanks but more commonly by gravity feed or pumping. Here, the remaining binder and liquid, as well as various additives and tinting colors, are incorporated. The finished product is then transferred to a filling operation where it is filtered, packaged and labeled.

The product remaining on the sides of the tubs or tanks may be allowed to drain naturally and the "cleavage," as it is called, wasted or the sides may be cleaned with a squeegee during the filling operation until only a small quantity of product remains. The final cleanup of the tubs generally consists of flushing with an oil-base solvent until clean. The dirty solvent is treated in one of three ways: (1) it is used in the next batch as a part of the formulation; (2) it is placed in drums that are sold to a company where it is redistilled and resold; or (3) it is collected in drums with the cleaner solvent being decanted for subsequent tank cleaning and returned to the drums until only sludge remains in the drum. The drum of sludge is then sent to a landfill for disposal.

Figure 8-33-1 is a flow diagram for oil base paint manufacture.

Water Base Paint and Ink

Water-base paints and inks are produced in a slightly different method than the oil-base products. The pigments and extending agents are usually received in proper particle size, and the dispersion of the pigment, surfactant and binder into the vehicle is accomplished with a saw-toothed disperser. In small plants the product is thinned and tinted in the same tub, while in larger plants the product is transferred to special tanks for final thinning and tinting. Once the formulation is correct the product is transferred to a filling operation where it is filtered, packaged and labeled in the same manner as for oil-base paints and inks.

As in the oil-base paint and ink operation, as much product as possible may be removed from the sides of the tub or tank before final cleanup starts. Cleanup of the tubs is done

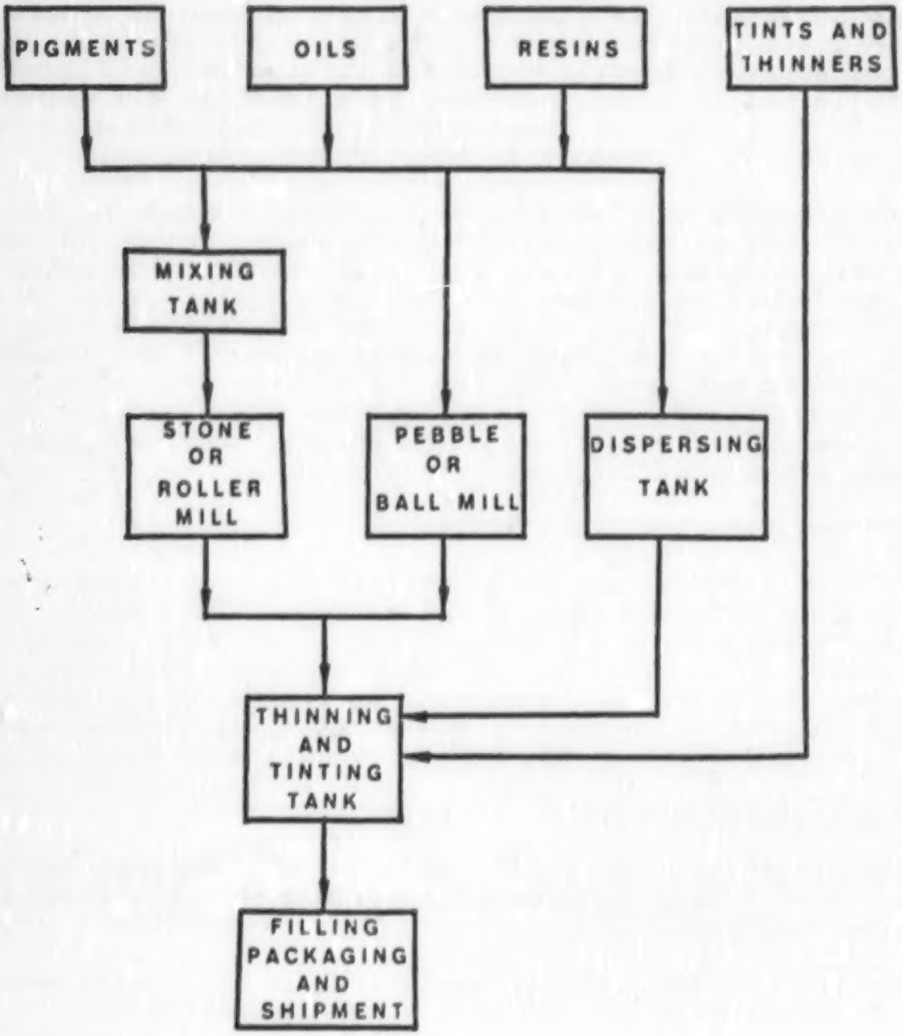

PIGMENTS
OILS
RESINS
TINTS AND THINNERS
MIXING TANK
STONE OR ROLLER MILL
PEBBLE OR BALL MILL
DISPERSING TANK
THINNING AND TINTING TANK
FILLING PACKAGING AND SHIPMENT

Figure 8-33-1

Paint and Ink Industry

Flow Diagram of Manufacturing Process for Oil-Base Paints simply by washing the sides with a graden hose or a more sophisticated washing device. The washwater may be: (1) collected in holding tanks and treated before discharge; (2) collected in drums and taken to a landill; (3) discharged directly to a sewer or receiving stream; (4) reused in the next batch; or (5) reused in the washing operation.

Allied products manufactured by the paint portion of the industry include putty, caulking compounds, paint and varnish removers, shellacs, stains, wood fillers and wood sealers. The manufacturing process for these products does not generally utilize water, except for some water-base stains and paint removers. The types of wastes generated in cleanup of equipment do not greatly differ from those generated in paint formulation. As these categories are generally low in water use and are very similar to paints, they have been considered as being in the same category.

4. Wastewater Characterization

Table 8-33-1 shows raw wasteload data for process water only. The process with the largest water usage is non-contact cooling water, which can account for up to 80% of the wastewater discharge. This should not be contaminated when operated properly. Wastewaters from cleanup operations, air pollution control equipment, and sanitary discharges account for a major portion of the remaining discharge flow.

5. Control and Treatment Technology

In-Plant Control - The use of modified washing methods, such as the use of high pressure nozzles, can reduce the amount of water discharged.

Another method for reducing wastewater is by reusing washwater, if the formulation of the next batch is compatible.

A third method of reducing wastewater is the use of dry cleaning procedures for handling spills and leaks.

Treatment Technology - The most common treatment schemes consist of either batch or continuous clarification basins or tanks with pH adjustment and coagulant feeds. In addition, many plants send their process wastes to scavengers for disposal, which totally eliminates wastewater discharge.

TABLE 8-33-1

Raw Waste Characteristics

Paint and Ink Industry

	Subcategories	
Parameter mg/l	Paint	Ink
BOD	60-1800*	60-2000*
TSS	40-11000 *	15-1200
COD	5000-8000*	200-3000*
pH	3.4-13.2*	5.6-11.6*
Iron	4-40*	0.6-2.2
Lead	1*-10*	0.3
Manganese	0-10	0-0.1
Zinc	0.3-10*	No Data
Oil and Grease	4-1000*	7-200*
Kjeldahl Nitrogen	0-200	No Data

* See Appendix 5 for parameters which may be inhibitory to biological systems.

1. General Industry Description

The Steam Supply and Noncontact Cooling Water industry includes all establishments engaged in the production or distribution of steam and heated or cool air,and the use of noncontact cooling water for steam supply and any other use. Steam is generally used for power generation, space heating, and process heating. Noncontact cooling water in other than power generating plants is used for product, process, equipment cooling and air conditioning. Wastes from the steam supply industry contain widely varying pH values, metals, corrosion inhibitors and dissolved and suspended solids. Noncontact cooling water waste streams contain corrosion inhibitors, slime inhibitors and dissolved and suspended solids. The Steam Supply portion of this industry is covered by Standard Industrial Classification (SIC) 4961. The Noncontact Cooling Water portion does not have a SIC classification.

2. Industrial Categorization

Major Category	Subcategory
Steam Supply	Continuous Wastewater Discharges Intermittent Wastewater Discharges
Noncontact Cooling Water	Thermal Discharges Chemical Discharges

3. Process Description

Steam Supply

Water and heat are added to the steam generating boiler to produce steam at the desired pressure and temperature. Water is normally treated before use in the boiler with the degree of treatment dependent upon the boiler operating conditions and the quality of the intake water.

The boiler consists of a series of tubes connected to two boiler drums: the steam drum and the mud drum. The water is heated by hot fuel gases as it passes through the tubes and exits as steam through the steam drum. Impurities collect in the mud drum and are periodically removed.

Wastewaters are discharged both continually and intermittently from a number of sources in the operation. Since steam may be lost in the cycle, make-up water which may require pretreatment is added to make it acceptable to the boiler. The higher the pressure and temperature of the boiler, the more stringent the make-up water quality requirements are. Water treatment consists of filtration, softening, and/or dissolved solids removal by ion exchange. Waste streams from the water treatment processes consist of filter backwashes, sludges from clarifiers, and brines from ion exchange regeneration. These wastes are generally intermittent.

Due to the continued evaporation of water within the boiler, buildup of dissolved solids occurs. To maintain total dissolved solids within allowable limits, a controlled amount of boiler water is blown down. The blowdown is usually continuous from the steam drum while blowdown from the mud drum is intermittent. Water used for steam generation is normally internally treated with chemicals to:

1) Prevent scale formation caused by hardness.
2) Provide pH control and oxygen scavenging to prevent corrosion.
3) Condition any sludge that may form.

The chemicals used for these purposes are di- or tri-sodium phosphate, ammonia, caustic, cyclohexylamine, sodium sulfite, hydrazine, and morpholine. The particular chemicals used appear in the boiler blowdown. In spite of internal water treatment, deposits accumulate in boiler tubes which, if allowed to go unchecked, would cause overheating and tube failure. To prevent this, boiler tubes are cleaned. The interval between cleanings normally varies from once a year to once in ten years. Scale deposits may include calcium, magnesium, phosphates, oxides of iron and copper, and, to a lesser extent, zinc, nickel, and aluminum. Common cleaning agents used are hydrochloric acid, citric acid, formic and hydroxyacetic acid, or solutions containing such chemicals as chelates, potassium bromate, phosphates, thiourea, ammonia, hydrazine, and caustic soda. The water containing the scaling materials and the particular chemical or chemicals used, constitute a waste stream.

The fireside of the boiler is also cleaned approximately once per year. The fireside is usually cleaned only with water, and the waste stream contains the slag buildup caused by the fuel gases.

Steam generation plants which utilize coal or oil or waste as fuel produce ash as a waste product of combustion. The ash can be bottom and/or fly ash. Bottom ash (from coal only) accumulates in the furnace bottom, while fly ash (from coal and oil) is carried over in the flue gas stream. Ash is handled either dry (pneumatic) or wet (sluicing). Wet handling of ash produces wastewaters. The storage of coal can produce a waste stream caused by rain runoff.

Noncontact Cooling Water

Noncontact cooling waters are used to accept heat from a process which requires cooling. Once through noncontact cooling systems result in both chemical and thermal waste discharges, while recirculating systems generate only chemical waste discharges.

In once through noncontact cooling systems, it is necessary to prevent growth of organisms in condenser tubes in order to maintain heat transfer surfaces in clean condition. This is normally accomplished by adding slug quantities of common biocides, such as chlorine or hypochlorites. These chemicals appear in the cooling water discharge stream, in addition to heat.

In a closed cycle cooling system where a cooling tower is used to dissipate the heat to the environment, the only waste stream generated is cooling tower blowdown, which contains dissolved solids and chemicals added to prevent scale buildup and slime growth. These chemicals include chlorine, hypochlorite, and compounds of chromium, zinc, and phosphate.

4. Wastewater Characterization

Table 8-34-1 contains the wastewater characteristics for the processes described above.

TABLE 8-34-1

STEAM SUPPLY AND NONCONTACT COOLING WATER INDUSTRIES
RAW WASTEWATER CHARACTERISTICS

Waste Parameter (mg/l)	Process Wastes						
	Boiler Steam Drum Blowdown	Boiler Mud Drum Blowdown	Ash Pond Overflow	Chemical Cleanings of Boilers	Coal Storage Runoff	Once Through Cooling Water Discharge	Cooling Tower Blowdown
Flow, GPD	1.4M-216M						3-300
Flow Type	C	B	C	B	B	C	C and B
TSS	0-600		700	150-2.5M	350	No Data	No Data
TDS	100-10M*	1M*-2m*	500	No Data	3500*	No Data	No Data
COD	10-1.4M*	60-1M*	No Data	20-3M*	No Data	No Data	No Data
pH	7-11*	7-11*	No Data	low & high	3	No Data	No Data
Chromates	0-7*		0	0-12*	No Data	No Data	0-30*
Total Nitrogen	0-25	3-10	2	No Data	No Data	No Data	No Data
Phosphate as P	0-80	0-20	1.3	0-4	No Data	No Data	0-30
Iron	0-80*	0.3-4	12*	2-1M*	0.5	No Data	No Data
Copper	0-2*	0.03-4*	0.2	0-200*	2*	No Data	No Data
Nickel	0-1.2	0.1	0.3	5*-75*		No Data	No Data
Zinc		0.05-0.5*	0.5*	5*-50*	1.5*	No Data	0-15*
Oil and Grease	Present	Present	Present	Present	Present	No Data	No Data
Chlorine, Free Available						Present	1

Notes:
M = 1,000
MM = 1,000,000
* See Appendix 5 for parameters which may be inhibitory to biological systems
B Batch Process
C Continuous Process

5. Control and Treatment Technology

In-Plant Control

Control technology to minimize wastewater discharges may involve process equipment changes. Equipment to improve the quality of the water to the steam boiler would reduce the boiler blowdown volume. Substitution of closed cycle cooling (cooling towers) for once through cooling systems can eliminate thermal discharges.

Treatment Technology

Metals can be removed from wastewaters by pH adjustment with lime to 8.5-9.5 which results in precipitation of the metal hydroxides. The precipitated metal hydroxides and the suspended solids can then be removed in a clarifier. Biocides can be eliminated by the addition of a reducing agent, such as sulfites, which reduce chlorine to chlorides.

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LIST OF REFERENCES

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Grain Mills	1. Grain Processing Segment	440/1-74-028-a
	2. Animal Feed, Breakfast Cereal and Wheat Starch Segment	440/1-74/039
Canned and Preserved Fruits and Vegetables	1. Apple,Citrus and Potato Segment	440/1-74-027-a
	2. Canned and Preserved Fruits and Vegetables	Contractors Draft (contract #68-01-2291)
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	2. Fishmeal, Salmon, Bottom Fish, Sardine, Herring, Clam, Oyster, Scallop and Abalone Segment	440/1-74/041
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	2. Primary Aluminum Smelting	440/1-74-019-d
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	2. Calcium Carbide	440/1-75-038
	3. Electrolytic Ferroalloys	440/1-75-038-a
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	2. Flat Glass	440/1-74-001-c
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Miscellaneous and Beverages	Miscellaneous Foods and Beverages	Contractor's Draft
Miscellaneous Chemicals	Miscellaneous Chemicals	Contractor's Draft

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